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EXPOSURE OF A FOOD CROP TO
TRICHLOROETHYLENE FROM A
CONTAMINATED AQUIFER
THESIS

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CONTAMINATED AQUIFER

THESIS

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Abstract

This research developed a methodology for assessment of the exposure of a mature corn crop to trichloroethylene from a contaminated aquifer. The methodology was then applied to the case of Hill AFB to determine the ability of the methodology to provide information about a specific exposure. There are currently several locations where ground water, contaminated with TCE originating from an Air Force facility, has the potential to expose food crops. Current procedure for estimating the risk to human health from this type of food crop exposure is focused on sampling the food product and lacks the information to predict where exposure problems are more likely to exist. A review of the potential exposure pathways from the aquifer to the crop was conducted. On the basis of this review, the exposures due to soil gas and irrigation were modeled. Empirical estimates were used to approximate the expected flux of soil gas vaporizing directly from the aquifer. On the basis of this approximation, the exposure in the air of the crop canopy was mathematically estimated. Analytical models were developed to simulate the amount of the contaminant reaching the crop from two different means of irrigation. The subsequent exposure once the contaminated irrigation water had reached the crop was modeled both in the air of the crop canopy and the soil phase near the root system. The methodology provided insights into which exposure pathways are more important than others and revealed some to be negligible. Information was also gained regarding the environmental parameters that are most influential in determining the amount of exposure.

EXPOSURE OF A FOOD CROP TO TRICHLOROETHYLENE FROM A CONTAMINATED AQUIFER

I. Introduction

Trichloroethylene is a solvent common to many commercial operations. Its wide use has included everything from degreasing fabricated metal parts to use as a general anesthetic in surgical procedures (Kimbrough and others, 1985:369). Past practices, such as inadequate disposal methods, have led to a problem with TCE contaminated groundwater. In fact, TCE is the most common organic groundwater contaminant and occurs at higher concentrations than any other organic pollutant (Marrin and Thompson, 1987:21). With its numerous and widely varied operations, the Air Force has found that it has its own problem with TCE contamination (Gross and Termaath, 1985:119). One of the consequences of this contamination is the potential for the contamination of food crops, whether in commercial farms or private garden plots, and the subsequent exposure of humans. At McClellan Air Force Base, TCE originating from Air Force operations has been detected in off-base private wells that are being used to irrigate garden plots (ATSDR, 1994:33). Hill Air Force Base has a similar problem with irrigation of food crops using groundwater contaminated by TCE from the base (Radian, 1994:S-2).

The current approach to identifying crop exposure problems focuses primarily on sampling food products for the presence of chemicals. Very little has been done to examine the ways that organic chemicals are transported to and taken up by the crops. If more was known about the ways in which TCE becomes available to the plants for uptake, problems could be more readily identified or

anticipated and sampling and remediation efforts could be directed more efficiently.

The goal of this thesis is to develop a methodology for assessing the influence of environmental conditions on the potential exposure of a food crop to trichloroethylene from a contaminated aquifer. Specificly, the methodology will address a mature corn crop. This methodology will take the form of a series of environmental compartments which will be modeled to evaluate the maximum potential exposure. In order to assess the usefulness of the information obtained, these models will be applied to the example of Hill AFB.

Figure 1 shows the physical environment to be assessed. The first step is to evaluate the pathways TCE may take from the aquifer to the crop and the significant fates of TCE along those pathways. The TCE is assumed to start in the contaminated aquifer. It may be transported in vapor form within the air space of the soil to the area beneath the plants. From there, it potentially continues on to the air of the crop canopy to form an air exposure. Another pathway occurs when the contaminated water is pumped to the surface and used for irrigation. One of two irrigation methods might be used, spray irrigation or flood irrigation. Once it reaches the crop, the TCE may vaporize into the air of the crop canopy or it may leach into the soil surrounding the plant roots. The next step of the methodology will be to estimate these exposures in the air and soil.

After the development of the methodology, results associated with Hill AFB will be examined. Where actual data is not available, the conditions at Hill AFB will be approximated as nearly as possible. By examining the results from the models, the type of information to be gained, as well as its usefulness, will be ascertained.

This methodology will be a first step in better understanding situations where crop exposure to aquifer contaminants is a problem. Based on the information

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gained, sampling regimes may be developed more efficiently. The methodology may also reveal those situations where the exposure may be considered negligible.

The series of models may also provide information by which the risk to humans may be decreased. By assessing the significant factors which lead to crop exposure, the models will provide insight into ways in which potential problems can be corrected. By contributing information and understanding, this methodology will be a potentially valuable tool in identifying and decreasing the overall risk to human health.
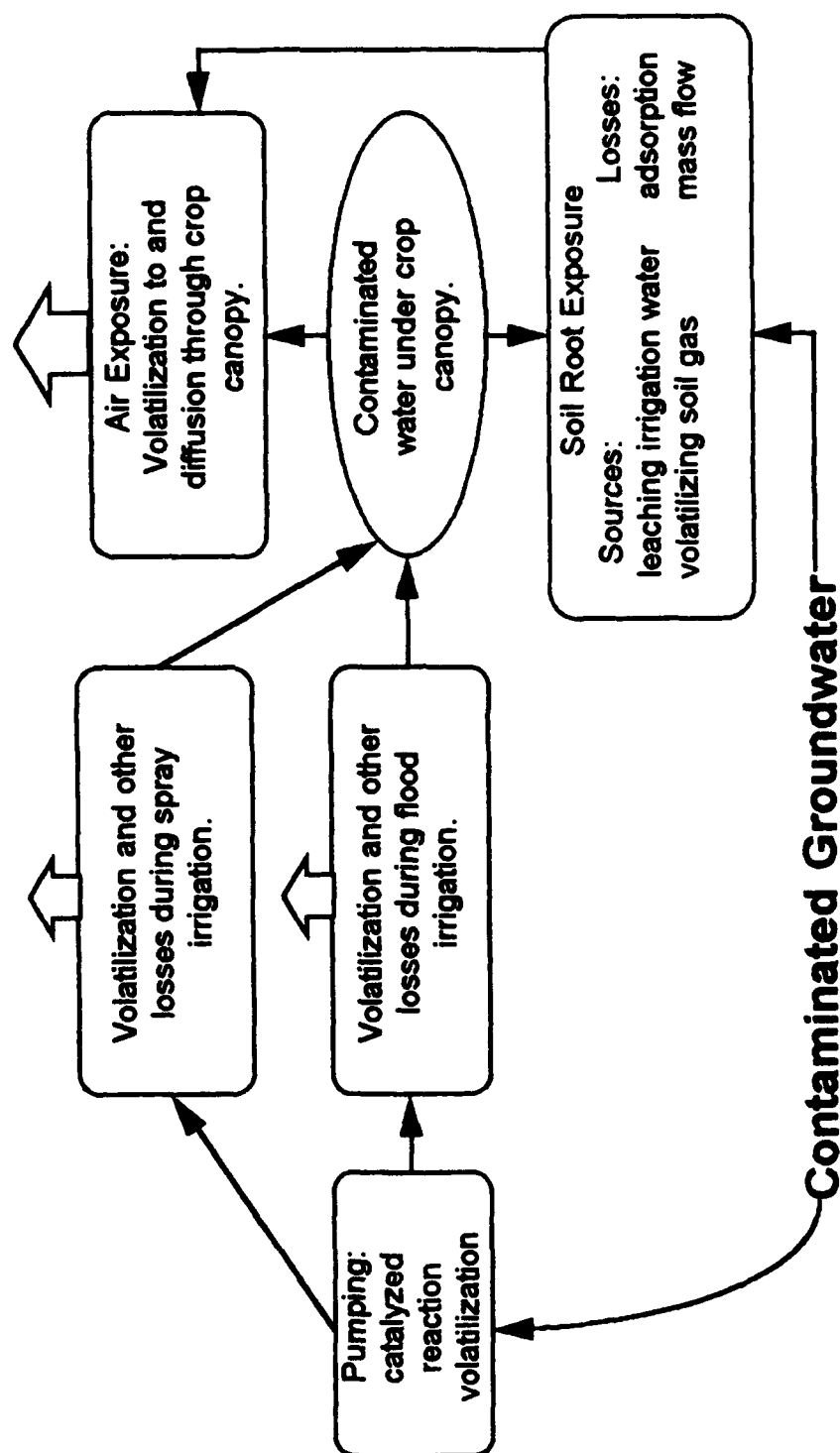
Figure 1: Compartmentalized model of TCE available to a food crop from a contaminated aquifer.

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II. Literature Review

Trichloroethylene

Chemical Properties. The chemical properties of TCE determine how it behaves in the environment. Some of the more important parameters used to describe the behavior of organic chemicals are the octanol/water partition coefficient, the organic carbon partition coefficient, vapor pressure, solubility, and Henry's Law constant. The values of these properties and others of importance are listed in Table 1. These properties not only serve as relative measures of a certain behavior but are also used to analytically describe and predict particular behaviors of interest.

Octanol/Water Partition Coefficient. The octanol/water partition coefficient (K_{ow}) is a measurement of the relative solubility of a chemical in octanol versus water. A large K_{ow} generally indicates a tendency to accumulate in soil, sediments, and the lipid phase of biological systems. On the other hand, a chemical with small K_{ow} tends to partition into the air or water (ATSDR, 1992:6-12). Trichloroethylene has a relatively low K_{ow} (log K_{ow} =2.29)(Bourg and others, 1992:359). Due to this low K_{ow}, bioaccumulation in the food chain is not thought to be a significant concern (Callahan and others, 1979:52-4). This small coefficient value also reflects the fact that TCE is weakly hydrophobic (Bourg and others, 1992:359).

Organic Carbon Partition Coefficient. The organic carbon partition coefficient (K_{oc}) measures the tendency of a chemical to be adsorbed by soil and sediment (ATSDR, 1992:6-12). This is a chemical specific parameter (ATSDR,

1992:6-11) but it may change dramatically with the particular properties of the individual soil (Domenico and Schwartz, 1990:443). Because of the strong dependence of K_{oc} the individual soil being dealt, a value is not given here. There is a strong correlation between K_{oc} and K_{ow} because partition between organic carbon and water is very similar to partitioning between octanol and water (Domenico and Schwartz, 1990:443).

Vapor Pressure. The vapor pressure of TCE is important because it indicates the tendency of the chemical to volatilize from the liquid phase to the gaseous phase. Chemicals with a high vapor pressure have the ability to move from liquid phase in the soil to the soil air phase where they may be quite mobile. The vapor-phase may be taken up by the plant below ground by the roots or it may volatilize to the ambient air and be taken up by the above ground portions of the plant (Ryan and others, 1988:2305).

The vapor pressure is the pressure which exists in the gas phase when the gas and liquid phases of the chemical are in equilibrium (Weast, 1985:F105). As temperature increases the vapor pressure will increase. On a molecular level, this is because that increases in temperature increase the average kinetic energy of the molecules and subsequently increase the number of molecules with sufficient kinetic energy to escape the liquid into the gaseous phase (Bodner and Pardue, 1989:G-15). The vapor pressure of TCE is 74 mm Hg at 20°C (Dilling, 1977:407).

The solubility of a chemical is a measurement of how much of the substance will dissolve into solution with a certain solvent and is normally described with water as the solvent. Solubility of non-ionic chemicals is mostly determined by the relative polarity of the solute and solvent. Like tends to dissolve like. For example, weakly polar solutes are most effectively dissolved by weakly polar solvents (Morrison and Boyd, 1992:32). The solubility of TCE in water has been measured

as 1.366 g/L at 20°C (ATSDR, 1989:33). This is considered a low solubility. It may be implied that this is because TCE is considered weakly polar or non polar and water is highly polar.

Henry's Law Coefficient. The Henry's Law coefficient (K_H) is a constant which measures the tendency of a chemical to volatilize from a solution. The molecular weight, vapor pressure, and solubility all come into play in determining how strongly the chemical is driven into solution relative to the gaseous phase, and they all help determine the value of this constant (ATSDR, 1992:6-9). If something happens to decrease the solubility of a chemical, such as a change in temperature, the change is reflected in this coefficient. In a similar manner, if the vapor pressure of the chemical changes, the tendency to volatilize from the solution changes. Once again, the Henry's Law coefficient reflects the new relationships (Bodner and Pardue, 1989:597).

In contrast to vapor pressure, which measures the pressure of the liquid, this coefficient indicates the partitioning concentrations between the liquid and gas phase at equilibrium. Analytically, Henry's Law can be expressed as:

$$C_g = K_H C_L$$

where C_g and C_L are the concentrations in the gas and liquid phases respectively. A substance with a higher Henry's Law constant moves to the gaseous phase. The Henry's Law constant for TCE is 1.18 (kPa m^3/mol at 25°C) For volatilization to be significant, an organic solvent should have a vapor pressure of 130 Pa or greater and a Henry's Law constant of 50 Pa m^3/mol, as TCE does (Bourg and others, 1992:360).

Transformation. The loss of trichloroethylene to degradation, reaction, or other transformation is important to knowing a compound's persistence in the environment. Whether or not it degrades under certain conditions determines

whether or not it makes it to the receptor, in this case the corn plant, and, if it

remains in the vicinity of the receptor, whether or not it accumulates. In the problem

under consideration,

Parameter	Standard Symbol	Value	Source
Octanol Water Partition Coefficient	K_{ow}	$\log K_{ow} = 2.29$	(Bourg and others, 1992:359)
Vapor Pressure		9.8 kPa at 20°C	(Dilling, 1977:407)
Aqueous Solubility		1.366 g/L at 20°C	(ATSDR, 1989:33)
Henry's Law Constant	K_H	$1.18 kPa\ m^3/mol$ at 25°C	(Bourg and others, 1992:360)
Adsorption Equilibrium Constant for TCE	K_d	11.7 mL/g	(Pavlosthis and others, 1991:277)
Gaseous Molecular Diffusion Coefficient	D	$7030\ cm^2/day$	(Peterson and others, 1988:576)
Molecular Weight TCE	M	130 g/mol	

Table 1: Summary of chemical properties of TCE.

there are several environments in which TCE is being examined and may be

degraded or react to form other chemicals. The air, unsaturated soil, and the

aqueous environments are all separate compartments in this model where this may

happen.

Reaction with hydroxyl radicals is the primary loss pathway for trichloroethylene in air (USEPA, 1985:1-1). Hydroxyl radicals form in the atmosphere in the following reaction involving ozone and water vapor:

$$O_3 + hv \rightarrow O(D') + O_2$$

$$O(D') + H_2O \rightarrow 2OH$$
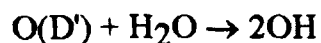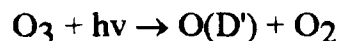
where hv represents ultraviolet light and O(D') is excited oxygen. By the above equations, it is apparent that the hydroxyl radicals are formed in the presence of sunlight (Godish, 1991:50) and the atmospheric lifetime of the hydroxyl radicals is on the order of microseconds (Hauser, 1994).

This is important in that the crop canopy, the air environment of concern, is assumed to not allow a substantial amount of sunlight in. It is doubtful, considering the atmospheric lifetime of the hydroxyl radicals, that any significant quantity of hydroxyl radicals would persist long enough to be transported to portions of the canopy not radiated by the sun. This is perhaps a conservative assumption because some sunlight would reach some levels of the crop below the initial canopy and some reactions would therefore take place. In the troposphere, half life of TCE has been estimated from 54 hours to 2 weeks(USEPA, 1985:3-6). No studies have been found which are applicable to an air environment which lacks complete ultraviolet light.

The second environment, the unsaturated soil environment, is even more difficult to quantify. A review of the literature has not uncovered direct and quantifiable indications degradation or other loss of TCE in the soil environment. This may be due to the inability to quantify an actual source of the TCE with sufficient accuracy as well as difficulty in quantifying loss pathways, such as partitioning into the soil. In essence, the necessary mass balances have not been established. Various studies that have attempted to estimate degradation in soil

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systems have postulated biodegradation as the most likely transformation process but have estimated it to be slow if present at all (ATSDR, 1989:91).

Flood irrigation often uses open trenches to transport the water to the plant. At that time the TCE is in a purely aqueous environment. There are no loss pathways which, in an aerated aqueous environment, are significant compared to volatilization (ATSDR, 1989:91).

Soil Gas Pathway

Sorption. Sorption is a term which refers in general to a situation where the soil matter in some way binds up the molecules of a contaminant. The two mechanisms which normally categorize sorption are adsorption and absorption. In adsorption, the contaminant physically adheres to the exterior surface of the sorbing material. In absorption, the contaminant is taken into the interior of the soil matter in a manner similar to the way a sponge would soak up water. In both cases the contaminant is no longer mobile, and its activity in the environment is inhibited. Sorbed chemical is also not available for uptake by the plant (Boesten, 1993:405). Hence, the sorption of TCE to soil matter has a primary role in determining the activity of the chemical in the soil environment (Chiou, 1990:152).

Soil has two solid phases which play a role in sorption, the mineral portion and the organic portion. The mineral content of the soil acts as a conventional solid adsorbent, and the soil organic matter acts as a partition medium, or absorbent (Chiou, 1990:118). Only a finite amount of water and contaminant can adsorb to the surface of a given amount of mineral. Water is more polar than TCE, and this increased polarity gives it a stronger tendency to be adsorbed (Chiou and others, 1985:1198). In the resulting competition, the moisture in the soil decreases the amount of TCE which can be adsorbed.

The moisture content of the soil is therefore an important factor in the mineral sorption activity of TCE, and mineral sorption becomes a less dominant mechanism as moisture content increases (Peterson and others, 1988:571). Because of this competition with the water, sorption of TCE in an unsaturated environment is quite different from sorption of TCE in a saturated environment (Peterson and others, 1988:571). Water competes so strongly for adsorption to the minerals that it can actually displace TCE from the mineral, and an increase in moisture content can cause a release of TCE (Spencer and others, 1982:20). The water content necessary to sustain plants, known as the wilting point is sufficient to displace the water from the mineral content and make partitioning to the soil organic content the dominant sorption mechanism (Chiou, 1990:148). The wilting point is the moisture content below which plants wilt and do not recover (Hartman and others, 1988:666). Thus, mineral sorption is not a controlling mechanism in a healthy agricultural environment.

TCE partitions into the soil organic content by forces typical to a substance going into solution, such as Van der Waals forces (Chiou, 1990:152). Van der Waals forces are the electrostatic interactions between molecules. Sorption by soil organics increases linearly with the TCE concentration. This is in contrast to sorption by the mineral portion, which is very nonlinear (Chiou and others, 1985:1200). As a result, sorption ranges from being highly linear to highly nonlinear depending on the relative dominance of mineral and organic sorption. The total adsorption activity of the soil/TCE system is affected by such things as the properties of TCE, TCE concentration, soil moisture content, and the soil properties, such as amount of mineral or organic matter (Spencer and others, 1982:17).

Flux Rates. Flux rate refers to the vapor flux from the contaminated aquifer to the crop environment through the soil atmosphere, or soil air space. This flux

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continues to the canopy and on to the atmospheric sink. There are several important pieces in this flow process. The first is the volatilization of the TCE from the contaminated aquifer to the soil air. The second is the transport of the vapor through the porous soil to the soil/air interface. From the soil/air interface the TCE diffuses into the crop canopy and thus becomes the first of the two exposure pathways being examined.

The initial step in this pathway is the volatilization of the TCE from the contaminated aquifer to the soil atmosphere. One determinant in this process is the amount of contaminant in the capillary fringe (Marrin, 1988:741). The capillary fringe is a saturated zone over the aquifer. Water is drawn up into this zone by the capillary attraction of the small pore spaces in the soil (Fetter, 1988:91).

Capillary attraction is the slight negative pressure which develops in the pore spaces in contact with the water (Domenico and Schwartz, 1990:89) due to the molecular attraction between the soil particles and the water (Fetter, 1988:91). At the capillary fringe the chemical can come into contact with the air and volatilize. It has been hypothesized that the chemical may move up through the capillary fringe by a combination of dispersion and molecular diffusion. In addition, water table fluctuations may greatly increase the amount of volatilization (Marrin, 1988:741). TCE is more dense than water and, tending to sink, may be found in higher concentrations progressively lower in the aquifer (USEPA, 1992:1). A decrease in the water level may bring the capillary fringe into contact with this higher concentration and allow greatly increased volatilization.

After vaporizing from the aquifer, the vapor phase TCE is in the soil gas phase in the unsaturated soil environment. In general, movement of vapor in the unsaturated zone is attributed to molecular diffusion (Bishop and others, 1990:257).

Molecular diffusion is the spreading due to random molecular motion and collisions (Jury, 1986:135). Flux of a gas due to diffusion can be expressed as:

$$F= -D\ dC/dz$$

and is this is known as Fick's First Law. F is the mass flux per unit area per unit time. D is the diffusion coefficient in units of area per unit time. dC/dz is the concentration gradient of the vapor. The negative sign indicates that the flow is from greater to lesser concentrations (Fetter, 1988:390). Transport by diffusion implies that the concentration in the soil gas would increase with depth and with proximity to the larger concentrations of the source. This has been observed in at least one case study (Marrin and Kerfoot, 1988:741).

Whether by directly influencing the diffusion coefficient of the chemical or by impacting the transport in some other way, many elements can affect the rate of transport in the soil gas phase, such as:

- the porosity of the soil
- the Henry's Law properties of TCE
- the adsorption to the soil
- the water content of the soil
- the evaporation of water content
- the variations in the soil composition

All of these factors combine to determine the amount of chemical available and the rate at which it is transported through the soil.

The porosity of the soil is defined as the amount of air space in the soil matrix and is a property which is characteristic of the soil type. It is defined mathematically as

$$\phi = 100\ V_v/V$$

where ϕ is the porosity in percentage, V_v is the volume of the void space in a unit
volume of soil, and V is the unit volume of soil with both the solids and the void
space (Fetter, 1988:63-64). This same property is often referred to as bulk density,
which is just the antithesis. As bulk density increases, porosity decreases and vice
versa. Porosity affects the rate at which vapor chemical is transported by
determining the cross sectional area available for diffusion. It also increases or
decreases the path length that the diffusing molecules must travel by determining the
amount of solids per unit volume that the vapor must go around. Porosity can be
incorporated into Fick's Law by a tortuosity factor. This is expressed as:

$$J_v = -\eta\ D\ \partial C_g\ /\ \partial z$$

where J_v is the vapor flux. η is a tortuosity factor which accounts for changes in
cross sectional area and path length due to changes in porosity.

Chemicals in the soil environment are governed by Henry's Law and its
implications for volatilization rates (Jury(b), 1986:159). The Henry's Law
properties of the chemical vary with environmental factors, such as soil temperature.
This may be most important at the capillary fringe where the chemical is initially
vaporizing.

Adsorption is important in that it decreases the amount of chemical which can
be transported to the surface and subsequently to the canopy environment (Jury(b),
1986:167). It forms an additional manner in which TCE may be lost and not expose
the crop.

Water content has several potential effects and these effects may be
contradictory. Soil moisture content will tend to decrease the transport of TCE to the
surface. Water content fills the pore spaces and decreases the amount of air space
within the soil available for diffusion (Jury, 1986:136). If water is evaporating

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within the soil matrix it may carry TCE with it by mass flow and cause an increase in the transport of the contaminant. This effect may be less for TCE than for other chemicals due to its relative insolubility (Spencer and others, 1982:21). Water evaporation at the surface and increased use of water by plants may cause an increase in the gradient of water vapor and a subsequent increase in diffusion of water vapor (Taylor and others, 1976:629). The reasoning is apparent by observation of Fick's Law as diffusion increases proportionally with the concentration gradient. This increase in the gradient due to evaporation is known as the "wick effect" (Spencer and others, 1982:22).

Correlation with Groundwater Concentration. While a significant amount of research has been accumulated on flow in saturated soils, relatively little is known about contaminant flow in soil gas and other unsaturated systems (Peterson and others, 1988:571). The variations in subsurface conditions, many of which are difficult to characterize, make quantitative relationships between a groundwater contamination and a soil gas contamination difficult to establish (Bishop and others, 1990:257). A review of the current literature has uncovered no predictive models of this environment. Several efforts have been made to statistically correlate groundwater contamination to soil gas contamination, and only order of magnitude relationships have been established (Bishop and others, 1990:257).

Soil-Air Interface. Once the TCE reaches the surface, volatilization is dependent on the vapor pressure of the chemical and its rate of movement away from the surface (Spencer and others, 1988:504) At the soil surface, the atmosphere generally has some turbulence which removes the TCE rapidly but, adjacent to the surface, there is a stagnant boundary through which the vapor must move by molecular diffusion (Jury, 1986b:161). Rate of diffusion through this stagnant layer is an important and possibly limiting step in the volatilization to the crop canopy.

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Precipitation tends to decrease volatilization because the water tends to move chemicals away from the surface by mass flow as it penetrates down through the soil. Irrigation with uncontaminated water has an effect similar to that of precipitation (Jury, 1986b:169). Irrigation and precipitation are important limiting factors on the volatilization of soil gas.

Numerous emperical models exist for predicting the volatilization of soil incorporated chemicals. Much of this work was accomplished for the purpose of characterizing the behavior of pesticides in the soil environment. Unfortunately, many of the parameters used in these model have to be determined experimentally and are not available for TCE. The models were developed and tested for agricultural chemicals, and TCE, lacking agricultural use, was not included in the studies.

Volatilization Related Fates

Volatilization From Ponded Water During irrigation with contaminated groundwater, a certain amount of TCE will be residual in the water after it reaches the crop canopy, and the water would be expected to pond for a period of time. During that time, the TCE will be transferred into the air of the crop canopy. Volatilization of TCE from a body of water can be described by a two layer model as shown in Figure 2.

The liquid film and gas film parts form the interface. The films are assumed to be stagnant, and therefore molecular diffusion is the primary mechanism for movement of the chemicals to or away from the interface (Liss and others, 1974:181). These diffusion coefficients have been evaluated for TCE. The bulk gas phase and bulk liquid phase are part of the main body of atmosphere or water. Movemert of the chemical in this phase is controlled by turbulence and molecular diffusion. Where turbulence is significant, it would be the dominant mechanism. In

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Turbulent and Molecular Transfer          ↑    Bulk air phase
                                          │

─────────────────────────────────────────────────────────────
Gas film                                   ↑    Molecular Transfer
─────────────────────────────────────────────────────── Interface
Liquid film                                ↑    Molecular Transfer
─────────────────────────────────────────────────────────────

Turbulent and Molecular Transfer          ↑    Bulk liquid
                                          │     phase
```
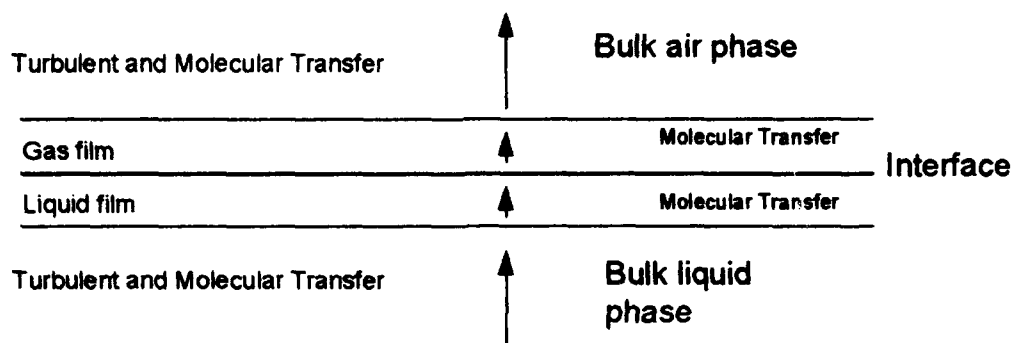
Figure 2: Two-layer model of a gas-liquid interface (Liss and others, 1974:181)

the case of water which has ponded under the crop canopy, turbulence will probably be negligible. The volatilization of the chemical requires that it first be transported to the liquid film layer, and it must then diffuse through the interface. At the interface the volatilization is controlled by Henry's Law (Spencer and others, 1988:505). The two rate controlling mechanisms are diffusion in the films and volatilization at the interface. The slower of the two mechanisms will control the rate at which the contaminate enters the atmosphere (Mackay and Wolkoff, 1973:611). This does assume that the transfer of the chemical is not rapid enough to cause depletion of the chemical near the liquid film. Contaminates that have a high vapor pressure tend to be limited in their volatilization by the diffusion through the liquid film as the transfer at the interface occurs more readily (Mackay and Leinonen, 1975:1178). One of the unexpected aspects of the volatilization of a dilute solute such as TCE in water is that the chemical will evaporate more rapidly than the water solvent even though the concentrations are within the solubility limits of the chemical (Dilling and others, 1975:833).

Another, slightly more complex situation where volatilization occurs in the problem under review would be the flow in the open ditch associated with transport to the crop during flood irrigation. Volatilization has been studied empirically

under many specific aqueous environments. They are distinguished by the factors which control the rate at which the TCE, or other solute, vaporizes. Such factors may include the following (Chiou, 1990; Liss and others, 1974; Barrio-Lage and others, 1987; Mackay and Leinonen, 1975):

Depth: The depth of the solvent determines the maximum distance which the solute will have to be transported to reach the liquid film.

Surface Area: The surface area of the solvent determines the size of the interface available to take part in the transfer.

Air Flow: If the air flow in the bulk air phase is not sufficient to prevent a significant vapor pressure from developing, the vaporization will be limited according to Henry's Law.

Turbulence: Turbulence in the bulk liquid prevents depletion of the chemical near the liquid film from limiting the rate of volatilization.

Diffusion Coefficient: The rate at which a chemical diffuses through the air and gas film layers can control the rate at which the chemical is transferred to the air.

Chemical Properties: The specific properties of the chemical, such as its Henry's Law constant and vapor pressure are, as stated previously, important in determining the rate of vaporization.

Because of these distinguishing elements, studies may, for example, measure one rate of volatilization for a solute in a vessel stirred at a certain rate and a very different rate for volatilization from a lake.

Aeration and Volatilization. Spray irrigation has the unique aspect of propeling the water through the air in droplet form. This act provides a unique opportunity for the TCE to vaporize and to be lost to the troposphere. Nearly all of

the information available about the behavior of TCE under these circumstances was collected for the purpose of studying exposure in an indoor environment from residential use of contaminated water, especially in a shower.

One of the most important considerations in the volatilization from drops is the drop size. Drop size is important because it controls the surface area of the interface between the liquid and the air phases (Giardino and others, 1992:1602). The amount of volatilization is also impacted by the chemical concentration in the gas form surrounding the drop, as might be expected from Henry's law.

The residence time of the drop in the air controls the amount of time the chemical has to vaporize before the drop reaches the end of its trajectory and changes phase (Giardino and others, 1992:1603). The most complex element may be the mass transfer coefficient. This is analogous to the transfer through the liquid film phase of the simple air/water interface in Figure 2 above. It is often treated as a resistance to volatilization.

There are several theories which attempt to explain the conditions of the drop and how the chemical interfaces with the surrounding air. These theories range from turbulent conditions within the drop to a drop which oscillates and changes shape during oscillation. Drop size is often a parameter in theoretical attempts to estimate the mass transfer coefficient (Altwicker and others, 1988:329). It is noteworthy that for chemicals with a high Henry's Law constant, such as TCE, McKone and Knezovich (1991:836) found the transfer efficiency to be a strong function of the rate of diffusion in water and not a function of temperature. In addition, Altwicker (1988:331) concludes that transfer to the gas phase is not velocity dependent despite the velocity dependence of most of the theories which attempt to explain the transfer.

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Pumping Losses

Prior to being used for irrigation purposes, water must be raised from the aquifer. This is typically done with one of a wide variety of pumps. A seemingly limitless number of parameters have been studied as to how they impact the concentration of TCE which is delivered by the pumping system. These include everything from pumping rate to the type of piping used. The original intent of these studies was to study the representativeness of samples taken for monitoring purposes, and the equipment being evaluated is quite different than that which would be used for residential or commercial water needs.

Many pumps lift the water by creating a negative suction. From Henry's Law, this might be expected to cause a volatile compound to enter the air phase. Pearsall (1987:64) found that this was not the case for lift heights of up to 24.5 feet. Ho (1983:586) concluded that this pressure drop did cause a loss of TCE at lift heights greater than 16 feet and that it increased with increasing lift height.

Pumping rate is often cited as an important factor in determining the amount of TCE in the water which is delivered. Ho (1983:586) found that increased pumping rates lead to significant losses of TCE but did not describe a potential causality.

The materials used in the pumping system may also be important in determining the amount of TCE which is delivered. For example, metals strongly adsorb organic compounds and act as a catalyst in some reactions (Pettyjohn and others, 1981:181). Many plastics will adsorb organics as well (Pettyjohn and others, 1981:181). However, these losses have not been quantified well enough to include them in this model.

A review of the available literature has not produced quantifiable losses which may be extrapolated to a typical irrigation scenario. This may be an

important blind spot in the current state of the research. The result of the handling of TCE by pumping and irrigation equipment, such as evaporation or catalyzed reactions, could have significant implications for assessments of risk to human health.

Behavior Under the Crop Canopy

The behavior of the contaminated irrigation water once it is within the crop canopy will take two important forms. Part of the water, along with the TCE, will evaporate into the air where the above ground portions of the plant will be exposed. In a similar manner, part will leach into the soil where it will expose the plant roots.

In the air of the crop canopy, the most applicable study is that of Parmele (1972). This study estimated pesticide fluxes by assuming that the diffusivity, or rate of diffusion, of the chemical is the same as the diffusivity of water vapor. In the case of an adult corn crop, the diffusivity was determined by distributing the wind drag into the crop canopy. The effect is an estimate of the turbulence under the vegetation due to wind above the vegetation. After vaporization, this diffusion of the TCE up through the crop and to the troposphere will be critical to determining the amount of accumulation.

The TCE tainted water will also leach into the soil. In the literature, _infiltrate_ normally refers to the rate at which ponded water enters the soil. _Leaching_ normally refers to the downward transport of water which is already in the soil. The fate of TCE is impacted by several activities:

-Uptake by the crop.
-Infiltration into the soil.
-Mass flow with the water.
-Partitioning into the soil.

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Absorption by the crop is a potential loss pathway for organic chemicals (Ryan and others, 1988:2307). Although the uptake by the plant may be an important fate of the TCE, such issues are beyond the scope of this thesis. Assuming no losses to plant uptake constitutes a conservative assumption for a model which is estimating the amount of TCE in the soil or air.

The rate of infiltration into the soil determines how long the water will be ponded on the surface where it volatilizes much more quickly. It is affected by the rate at which water is applied, the moisture content of the soil at the start of irrigation, and the properties of the soil. The infiltration rate is higher for soils with lower initial moisture content. As infiltration continues and the soil becomes saturated, the rate of infiltration becomes slower and approaches the rate associated with saturated soil and the saturated hydraulic conductivity (Letey and Oddson, 1972:402). The hydraulic conductivity is a coefficient of proportionality which describes the rate at which a fluid will move through soil and is characteristic of the properties of the soil (Fetter, 1988:78). This discussion assumes that the rate at which the water is applied is greater than the rate at which it can infiltrate the soil. If that is not the case, the rate at which the water is applied limits the rate at which the water can infiltrate the soil.

The TCE will be transported by mass flow, or carried with the water, and the movement of the water in the subsurface is important to the fate of the TCE (Letey and Oddson, 1972:402). After the water is in the subsurface it will penetrate to a certain depth. This depth is affected by the initial moisture content of the soil, the rate of application, and the properties of the soil (Letey and Oddson, 1972:402). Loss of water due to uptake by plants and evaporation to the surface can create a drying zone and lead to the wick effect discussed previously (Taylor and others,

1976:629). This upward movement of water can carry chemicals back toward the surface (Letey and Oddson. 1972:407).

The absorption by the organic content of the soil also helps to determine the fate of TCE. If the soil is irrigated with contaminated water, two factors determine the influence of absorption. The partition coefficient K_d is often used to describe the total mass of absorbed chemical as a function of the solution concentration, C. This can be written as:

$$S = K_d C$$

where S is the mass of absorbed chemical. This equation assumes that an equilibrium exists between the solution and absorbed concentrations. The rate at which the absorption, α, approaches equilibrium is also important (Oddson and others, 1970:413). The amount contaminant in solution and absorbed tends to remain highest near the surface and decrease with depth. These parameters determine the shape this concentration profile. If uncontaminated water is added later, the contaminant will move through the soil as a wave. The depth of the maximum concentration in this wave is influenced by K_d and tends to decrease as K_d increases. The α influences the magnitude of the maximum concentration in this wave.

III. Methodology

Exposure Due to Soil Gas

Likely Soil Gas Contamination. The best method currently available to estimate the soil gas flux which may be expected from a contaminated aquifer is from an examination of the existing case studies on TCE contaminated aquifers. The basis for comparison will be the factors which primarily determine the soil flux, such as amount of contamination, proximity of the aquifer to the surface, and the geology of the vadose zone.

The soil conditions at Hill AFB, the subject of the case study, are very heterogeneous and difficult to put into a specific category. The soils off-base where irrigation activities occur are silty sand with lower layers of silty clay (Radian, 1994:3-25). The contaminated aquifer ranges in depth from the soil surface to approximately 60 feet. Samples from the residential wells around Hill AFB measured concentrations up to 11.5 ppb TCE (Radian, 1994:3-35).

Several studies have examined the correlation between a groundwater contamination and soil gas concentration for TCE. Lappala and Thompson (1983) examined a site in the San Francisco, California area. However, the soils at the site range from fine sands to coarse gravels and are not comparable to those at the Hill AFB site (Lappala and Thompson, 1983:671). Runyon and Thompson (1987) examined a TCE contaminated site in Kansas, but insufficient information on the soil makeup is provided to draw analogies to the Hill AFB site. In addition, soil gas profiles necessary for obtaining information about the flux rates were not obtained. In Marrin and Thompson's (1984) study, two sites were examined, one in Tucson, Arizona and another site northern California. The vadose zone at the Tucson site

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was a "dry, gravelly-sand" and the aquifer was approximately 115 feet deep. Both of these features made it quite different from the situation in the case study. The site in northern California was a shallow aquifer, approximately 30 feet below the surface, and the vadose zone was characterized by "a soft, wet, sandy-silt soil" (Marrin and Thompson, 1984:173). This site was, among those studied, the most analogous to the one at Hill AFB. The flux of TCE calculated in the study for the northern California site is 12 μg/day per m^2 at a point where the concentration in the groundwater is 16 ppb (Marrin and Thompson, 1984:173). The soil gas profile resulting from this flux is given in Table 2.

Depth(ft)	TCE Concentration (μg/L)
Air Above Ground	.001
2	.003
3.5	.01
11	.6
14	2
20	3
26	16

Table 2: Soil gas profile at the northern California site (Marrin and Thompson, 1984:180)

Volatilization From Soil Gas. From the information in the study it is possible to assume that the transfer from the soil to the air is not rate limiting. If that had been the case, a build-up of contaminant would have been expected near the surface. This was not observed in the soil gas profiles (Marrin and Thompson, 1984:173). Therefore, the flux given in the study for the California site will be considered the flux which actually transfers to the air from the soil.

Transport of TCE Through the Crop Canopy. The development below seeks to analytically determine the expected TCE concentrations from the assumed level of soil gas flux. The approach will be to first develop a method of finding the effective diffusivity between the ground surface and any elevation within the crop canopy. With this diffusivity, the concentration gradients between the ground and any elevation can be found from Fick's Law. The concentration at the upper boundary of the crop canopy is assumed to be zero. With the concentration at the top zero, the concentration at the ground surface can be found from the difference in the concentrations at the two elevations. Calculation of the concentration differences, or gradients, between the ground surface and other elevations is then used to find the concentration at a given time and elevation.

Diffusivity in Corn Canopy. The diffusivities within a corn canopy were evaluated by Parmele (1972). The vapor transfer coefficient was calculated at the top of the corn over a 24 hour period by observation and calculation of the flux of water vapor. This coefficient was then distributed with decreasing elevation through the crop by a coefficient which expresses the diffusivity at that elevation as a fraction of the one at the top. Because the vapor transfer coefficient varies with time and the coefficient which distributes it through the various elevations varies with height, the diffusivity varies both with time of day and with elevation in the crop canopy.

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The distributing coefficient will be referred to as ψ. The values given by Parmele (1972) are shown graphically in Figure 3 and the specific data points are listed in Appendix 1.
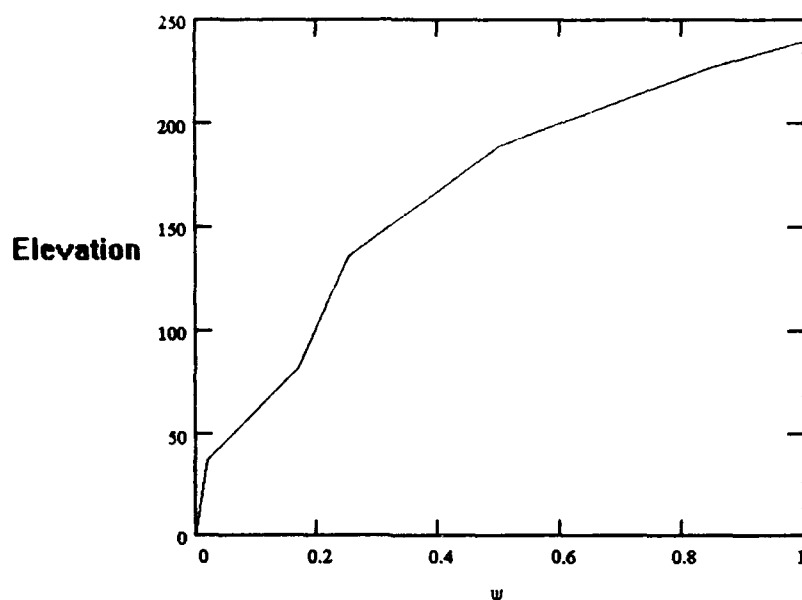
Figure 3: Relative diffusivity, ψ (cm^2/s), plotted as a function of height, x (Parmele and others, 1972:446)

Though Parmele does not explain the zero value of the distributing coefficient at the surface, it will be assumed to be some anomaly of the calculations he performed. If it were truly representative, it would, by Fick's Law, represent an impermeable layer at the surface. At the surface, the diffusivity will be assumed to equal the gaseous molecular diffusion coefficient for TCE. The gaseous diffusion coefficient for TCE is 7030 cm^2/day (Peterson and others, 1988:576). Values between the data points given by Parmele will be calculated by linear interpolation using the linear interpolation function of Mathcad edition 4.0. These interpolated values will be represented as $\psi(x)$.

The values of vapor transfer coefficient, K_z, have been adapted from Parmele (1972:444). All of the variables and symbols used in the model and its development

are summarized in Appendix 4. They are shown graphically in Figure 4 and the specific data points given by Parmele (1972) are listed in Appendix 2.
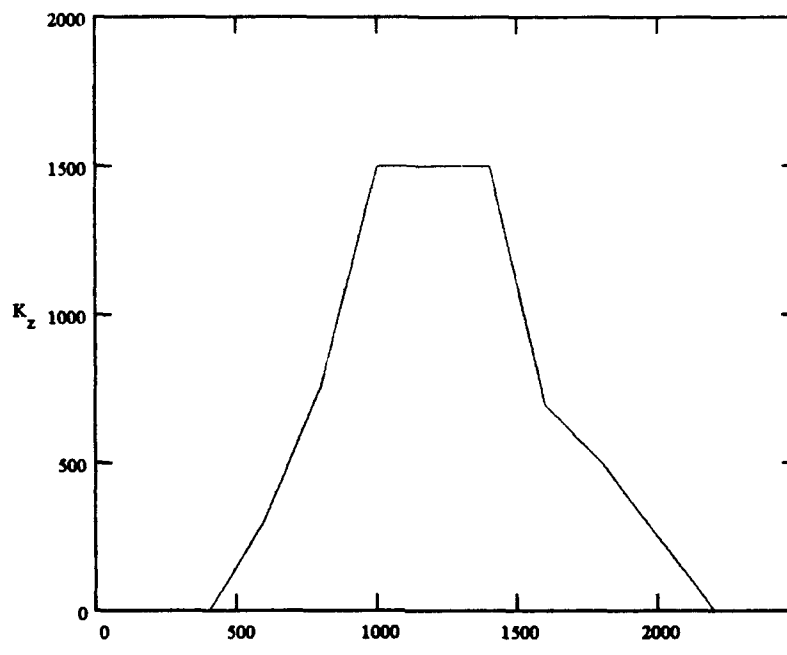
Figure 4: Vapor transfer coefficient, K_z (cm^2/sec), as a function of time, t (24 hr clock)

The vapor transfer coefficient is assumed to be zero during most of the night hours. The diffusivity at these times will be assumed in the model to be equal to the gaseous diffusion coefficient for TCE, as this would seem to represent the situation reasonably even under the most stable atmospheric conditions. The stable conditions of the night atmosphere represent a time when molecular diffusion dominates the physical transport mechanisms.

The diffusivity at a specific elevation and time can be found by multiplying the vapor transfer coefficient for time of day by the distribution coefficient for that elevation. The vapor diffusivity at the top of the canopy at time t will be represented

as $K_z(t)$. These values will be interpolated between data points. KA, the diffusivity at a specific elevation and time, can be evaluated as follows:

$$KA = K_z(t)\psi(x)$$

Effective Diffusivity. A point at any elevation sees a net diffusivity between itself and the ground surface. Regardless of the fluctuations in diffusivity with elevation, the concentration at the point is only a functional of the effective diffusivity(KE) between that elevation and the ground. In the problem being considered, the diffusivity varies continuously with elevation. This continuous variation is viewed here as a series of constant diffusivities in incremental layers. By analogy to hydraulic conductivity in saturated groundwater flow, the effective, or equivalent, diffusivity of these layers can by written as follows :

$$KE(x) = \frac{x}{\sum_{i=0}^{x} \frac{\Delta x_i}{KA_i}}$$

KE(x)=the effective diffusivity at elevation x
x   = the elevation being evaluated
Δx_i =the incremental layer assumed at increment i
KA_i = the diffusivity which is assumed constant through the incremental layer, Δx_i (Ritzi, 1993)

Liss (1974:181) has confirmed the validity of the analogy to groundwater flow and the use of the equation.

The development of the effective diffusivity assumes that the system is at steady state. With this assumption, the mass flux into the system is necessarily the same as the mass flux out of the system and the mass flux at any level.

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Evaluation of TCE Concentrations in the Crop Canopy. The diffusion of the soil gas through the crop canopy is a unique situation. The source of TCE is considered essentially infinite. For modeling the above ground exposure, the soil gas will be assumed to be a constant source.

Fick's Law can, assumining steady state diffffusion, be written (Couliette, 1994):

$$F = -KA\frac{\Delta C}{\Delta x}$$

ΔC = the change in concentration over Δx
Δx = the distance over which the change in concentration is being evaluated

Rearrangement of Fick's Law gives the following:

$$\Delta C = -\frac{F\Delta x}{KA}$$

With the assumption that the concentration is zero at the top of the corn, the change in concentration from the top of the corn to the bottom of the corn can be calculated. This is written as follows:

$$Csg_o = \frac{FX}{KT}$$

Csg_o = the TCE concentration at ground surface
KT = the effective diffusivity between the top of the corn and the ground
X = the height of the corn, assumed to be 240cm

Effective diffusivities are evaluated at various heights in the corn and, based on those diffusivities, the steady state concentration profile at a given point in time can be calculated. The concentration at elevation within the canopy can be written, by once again rearranging Fick's Law, as follows:

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$$Csg_x = Csg_0 + \frac{Fx}{KE_x}$$

Csg_x = the TCE concentration at x_i
x = the elevation being evaluated
KE_x = the effective diffusivity for level x_i

By substituting into the above equation for Csg_x, the model of equilibrium concentration profiles due to soil gas at time t can be written:

$$Csg(x,t) = \frac{FX}{KT} + \frac{Fx}{\left[\dfrac{x}{\displaystyle\sum_{i=0}^{x} \dfrac{\Delta x_i}{KE(i)}} \right]}$$

Irrigation Activity

Calculation of Water Requirements. The calculation of crop water requirements is based on a paper by Doorenbos and Pruitt (1977). All the necessary data has been obtained for Hill AFB and is summarized in Table 3. The month of July is assumed for the time of year.

The initial step in the calculation process offered by Doorenbos and Pruitt is the estimation of evapotranspiration. Of the methods discussed in the paper, the Blaney-Criddle was selected because the meteorological parameters it uses are readily available and the circumstances at Hill AFB, such as latitude and geography, meet the criteria established in the text. The relationship is as follows:

$$ETo = \sigma\left[p(0.46T + 8)\right]$$

ETo = evapotranspiration coefficient in mm/day

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T   = average temperature in °C

p   = average percentage of yearly daytime hours which occur during the time under consideration, tabulated by Doorenbos and Pruitt based on latitude and time of year

σ   = empirical adjustment factor based on climate (Doorenbos and Pruitt, 1977:3)

Parameter	Symbol	Value	Source
Average Temperature	T	24.4 °C	Internat Station Met Climate Summ
Hill AFB Latitude		41 North	Internat Station Met Climate Summ
Average Relative Humidity	RH	28.4	Internat Station Met Climate Summ
Average Rainfall	Pe	1.4 cm	Internat Station Met Climate Summ
Mean Wind Speed		7.6 KTS	Internat Station Met Climate Summ

Table 3: Hill AFB climatological data.

The evapotranspiration coefficient incorporates the influence of climate. All climate data was acquired from the CD ROM International Station Meteorological Climate Summary which gives data from the weather station at Hill AFB. Due to the empirical adjustment factor, σ, Doorenbos and Pruitt (1977) separate out the value, f, as follows:

$$f = \left[p(0.46T + 8) \right]$$

The evapotranspiration coefficient is then found based on data tabulated by Doorenbos and Pruitt (1977) based on minimum relative humidity, daylight hours, and wind estimates. The final number will be obtained from tabulated data

(Doorenbos and Pruitt, 1977:fig 1) assuming medium RH, mean daytime wind of 5 m/s, and medium to high sunshine hours (Doorenbos and Pruitt, 1977:3).

Another coefficient, the crop coefficient, incorporates the influence of the specific crop. The crop coefficient used here assumes sweet corn as would more likely be grown in a private garden. Together the two coefficients are used to calculate the crop evapotranspiration. The relationship is as follows:

$$\textbf{ETcrop} = \textbf{KcETo}$$

Kc = crop coefficient
ETcrop = crop evapotranspiration

The net irrigation requirement is given by the following relationship:

$$\textbf{In} = 30 \cdot \textbf{ETcrop} - (\textbf{Pe} + \textbf{Ge} + \textbf{Wb})$$

In = net irrigation requirement (mm/month)
Pe = average rainfall (mm/month)
Ge = groundwater contribution (mm/month)
Wb = water stored in the soil at the start of the time period (mm/month)

In the model, the water stored in the soil and the groundwater contribution will be assumed to be zero. The total volume required for irrigation is:

$$V = \left(\frac{10}{Ep}\right)\left[\frac{In}{(1 - LR)}\right]$$

V = total volume of irrigation required (mm/month)
Ep = percent efficiency of the irrigation method
LR = leaching requirement (fraction)

This equation is slightly different than the one given by Doorenbos and Pruitt (1977). Doorenbos and Pruitt multiply the net irrigation requirement by the acreage

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to get a cubic volume. Leaving this out gives millimeters of water, which is better suited to this model.

The irrigation system will be assumed to be 100% efficient. The leaching requirement coefficient increases the irrigation volume so that salts are leached away. The parameters necessary to calculate LR, such as "electrical conductivity of the soi ᵣation extract for a given crop appropriate to the tolerable degree of yield reduction," (Doorenbos and Pruitt, 1977:77) are not available. The tabulated data in the text has been used to arrive at an assumed value of 0.149. This is an approximate upper bound on LR and therefore maximizes V. Maximizing V maximizes the mass of TCE applied to the crop, and, therefore, is a conservative estimate.

Parameters	Symbol	Value	Source
Percentage Yearly daytime hours	p	33%	(Dorrenbos, 1977:Table 1)
Crop Coefficient	Kc	1.05	(Dorrenbos, 1977:Table 21)

Table 4: Parameters in model of irrigation requirements.

Losses During Spray Irrigation. One method of delivery of water modeled was spray irrigation. The model treated the aeration of the water during irrigation as a major loss of TCE to the troposphere. Any TCE volatized before reaching the ground was assumed to be unavailable to the corn crop. Giardino (1992) examined three models of losses from a shower spray. The models estimate a mass transfer coefficient and use that coefficient to calculate the concentration remaining in solution. The model used here was chosen because more of the parameters utilized

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are available and because in the experimental study by Giardino (1992) the error it demonstrated consistently underestimated volatilization during spraying. This will allow the model to remain conservative. The other models examined by Giardino (1992) occasionally overestimated the volatilization.

The mass transfer coefficient is given as follows (Giardino and others, 1992:1602):

$$K_L = \frac{.00375V_d}{1 + (\mu_d / \mu_a)}$$

K_L = the liquid phase mass transfer coefficient
V_d = the velocity of the water drop
μ_d = the viscosity of water
μ_a = the viscosity of air

The constants used in the calculation are summarized in Table 4. Utilizing this K_L, the concentration remaining in solution can be written as follows:

$$C_{L1} = C_0 \exp\left[-K_L \left(\frac{6}{d}\right) t_d\right]$$

C_{L1} = the concentration of TCE after it reaches the ground
C_0 = the initial concentration of TCE in the irrigation water
d = the drop diameter
t_d = the residence time of the drop in air

This is slightly different from the equation given by Giardino (1992). In this model, the air flow will be assumed to be sufficient to make the concentration of TCE surrounding the drops negligible. This assumption is justified by a shower study by McKone and Knezovich (1991) where the transfer efficiency did not change significantly with shower length (McKone and Knezovich, 1991:835). Longer showers would have had increasing gaseous concentrations of TCE around

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the drops. Based on this assumption, the gaseous concentration surrounding the drops in the original model given by Giardino was set to zero and the equation written accordingly.

Some of the parameters used in the spray model will have to be assumed. The study presenting the model is for a shower spray, and the drop diameter and residence time will differ from that of spray irrigation equipment. The drop diameter will be assumed to be .25 cm. This is within the range for which the model is still valid but larger than most of the drop sizes observed by Giardino (1992). The longer trajectory required of a spray irrigation system would be consistent with a larger drop size(Giardino and others, 1992:1603). Larger drops also tend to be less efficient at volatilizing the TCE, and it is therefore a conservative assumption (Gillham and Rao, 1990:493). The velocity is assumed to be 507 cm / s. This is the velocity found by Giardino (1991) for a 10 L / min shower spray.

The residence time will be approximated by the following trajectory equation (Serway, 1986:61):

$$t_d = \frac{V_d \sin(a)}{g}$$

a = initial angle of trajectory (assume 30°)
g = acceleration due to gravity (980 cm / s^2)

This is a rough estimation where the frictional forces due to air have been neglected. Based on the values already assumed, t_d is calculated to be .26 sec.

Losses Prior to Flood Irrigation. The irrigation water would likely be transported to the corn crop by flow through a culvert. Any TCE which volatilizes while in the culvert is assumed to be lost to the troposphere where it cannot expose the corn crop. One method of estimating the rate of volatilization is to estimate exponential decay rate of the TCE concentration in the aquifer. Based on that rate,

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Parameter	Symbol	Value	Source
Viscosity of Water	μ_d	1.0×10^{-3} N·sec / m^2	(Serway, 1986:333)
Viscosity of Air	μ_a	1.78×10^5 N·sec / m^2 (at 15 °C)	(Kuethe and Chow, 1986:518)

Table 5: Constants used in spray model.

the amount of time that the water takes to reach the field can be used to directly calculate the amount of TCE which remains when the water reaches the crop. Chiou (1979) gives a direct formulation of the mass transfer rate. The mass transfer coefficient is given by:

$$ k = \alpha\beta \ K_H \left(\frac{M}{2 \pi RT} \right)^{\frac{1}{2}} $$

k = mass transfer coefficient from water (cm/s)

K_H = Henry's law constant (dyne-cm/g)

M = molecular weight of the solute (g/mole)

T = temperature (°K)

β = coefficient which is a function of air flow (unitless)

α = coefficient which is a function of the liquid turbulence (unitless)

R = universal gas constant (J / mole °K)

Chiou evaluates α and β for a number of situations. Converting the units of the Henry's constant for TCE gives 1.07×10^5 dyne-cm/g under the following assumptions:

-K_H for TCE is 1.18 kPa m^3/mol at 25°C

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-dyne = 1 g cm / s2 (Weast, 1985:F-77)

-1 Pascal = 1 N / m2 (Serway, 1986:317)

For this Henry's constant and unstirred water, Chiou indicates an α of .9 (Chiou, 1979:235). The α for unstirred water is used under the assumption that the flow in the culvert is laminar or non-turbulent. Using the α for turbulent flow would give a larger evaporation rate and would therefore be a less conservative assumption.

Chiou (1979) also indicates a β for TCE evaporating into still air as 1.83×10^{-5}. The β for still air is used so that the estimate is conservative under even the most stable atmospheric conditions. Both of these coefficients are unitless. The transfer coefficient can be used as a decay rate and the calculation of a concentration is as follows (Masters, 1991:72):

$$C_{Li} = C_0 \exp\left(\frac{-kt}{L}\right)$$

$C_0 =$ the initial concentration of TCE
$t \ \ =$ the time that the water takes to reach the field

Time in the equation can be replaced by the distance traveled divided by the velocity of the water. The equation used in the model will be:

$$C_{Li} = C_0 \exp\left(\frac{-kl}{V_w L}\right)$$

$l \ \ =$ the distance traveled from well to field
$V_w =$ the velocity of the water in the culvert

The velocity of the water will arbitrarily assumed to be 1 m/s, and the distance will be assumed to be 1000 meters.

<u>Estimation of Root Exposure Due to Irrigation.</u>

<u>Estimation of Infiltration Rate</u>. As noted earlier, the infiltration rate starts at a rate dependent on the initial soil conditions, and decreases to the rate of the saturated hydraulic conductivity. This initial infiltration rate is not currently well defined and a review of the literature has not found an analytical model to portray it. This model will assume that the infiltration rate is constant at the saturated hydraulic conductivity. The saturated hydraulic conductivity will be assumed to be 10^{-3} (cm/sec). This is the low end of the hydraulic conductivities that might be expected for a silty sand such as are present at Hill AFB. According to Darcy's Law, the average linear velocity under these conditions will be:

$$V_z = \left(\frac{K}{n_e} \right) \frac{dh}{dz}$$

In this case, hydraulic potential, dh/dz, is the depth of the ponded water. The variables K and n_e are the hydraulic conductivity and the soil porosity respectively. The soil porosity will be assumed to be .6, which is a typical number for a silty sand (Fetter, 1988:67).

In the model for the penetration of the contaminant, the amount of time during which the contaminated irrigation water is infiltrating the surface represents the parameter t_0. The model will assume weekly irrigation. This can be evaluated as follows:

$$t_0 = \frac{Vper}{V_z}$$

The variable Vper is the depth of water applied during the weekly irrigation and is simply one fourth of the monthly net requirement. The rate of water application is assumed to be much greater than the rate of infiltration.

<u>Analytical Estimation of Penetration and Distribution</u>. Models describing the leaching of organic chemicals were designed for use with agricultural chemicals.

They assume a finite amount of surface applied chemical being leached by a large quantity of uncontaminated water. The case of contaminated irrigation water is unique in that the amount of organic applied is proportional to the amount irrigation water. The model used here assumes that a chemical dissolved in water enters the soil from time zero to t_0 and that after t_0 pure water enters the soil. In the development of the model, the time t_0 represents the time when the chemical on the surface is depleted.

The model was first developed by Oddson (1970). The development and re-evaluation of the equations is given by Letey and Oddson (1972). The depth into the ground is z. The coordinate system used has ground surface as z=0 and increasing z into the ground.

Letey and Oddson (1972) present two separate equations. The adsorbed concentration as a function is given by :

$$S(z,t) = K_p C_{L1} \exp\left(-\alpha K_p \frac{z}{V_p}\right) \int_0^{\tau\left(t-\frac{z}{V_p}\right)} \exp(-\tau) I_0\left[2\left(\frac{\alpha K_p z\tau}{V_p}\right)^{\frac{1}{2}}\right] d\tau$$

The boundary conditions are:

$$c(0,t) = C_{L1} \quad \text{for } 0 \leq t \leq t_0$$
$$c(0,t) = 0 \quad \text{for } t > t_0$$

These conditions state that a solution of concentration C_{L1} is applied until time t_0 and, after that time, the concentration applied is 0. I_0 is the modified Bessel function.

A condition for this specific equation is that:

$$S(z,t) = 0 \quad \text{for } 0 \leq t \leq z / V_z$$

This condition simply states that the adsorbed concentration at point z is zero before the wetting front reaches it.

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The result of this equation gives the adsorbed concentration, in the same units of C_{L1}, at any given time and point. The equation is not valid for time after the infiltration of contaminated water has stopped. Letey and Oddson give a modified form of the equation for time after t_0 which will be used to investigate the impact of rain. The development of the equation assumes that pure water is entering the soil after t_0 as would be the case for rain.

The coefficients α and K_d are the adsorption rate constant and the adsorption equilibrium constant respectively. K_d is readily available and is listed Table 1 for TCE. The transformation of K_d to the K_d used in the equation is direct and will be discussed below. Care must be taken as it is dependent on some of the characteristics of the soil. The value used here is one experimentally determined by Paviostathis and Jagial (1991). It has the advantage that the soil it is based on is well described in the study and the soil is reasonably close to that of Hill AFB. Several other soil parameters will be taken from the study by Paviostathis and Jagial (1991). Taking the parameters from an actual soil has the advantage of knowing that the parameters assumed do coexist in an actual soil and therefore do not conflict.

The α describes the rate at which the equilibrium between the sorbed and solution concentrations reach equilibrium. Mathematically it can be stated as:

$$\frac{\partial S}{\partial t} = \alpha(K_p C - S)$$

S is the sorbed concentration and K is the partition coefficient at equilibrium. At equilibrium the rate of change of the sorbed concentration goes to zero as $S = K_p C$. Currently sufficient data is not available to calculate a specific α for TCE in a given soil. None of the sorption studies found evaluate the necessary rate information. Letey and Oddson did provide a range of values, .033 to 5.09, which have been estimated for various soils and organic chemicals. This range will be used to observe the influence on the depth and concentration of the penetrating contaminant.

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The concentration in solution is given by:

$$C_s(z,t) = \frac{S(z,t)}{K_p} + C_{L1} \exp\left(\frac{-\alpha K_p z}{V_p}\right) \exp\left[\alpha\left(\frac{t-z}{V_p}\right)\right] I_0\left[2\left(\alpha^2 K_p z \frac{t-z}{V_p^2}\right)^{\frac{1}{2}}\right]$$

This equation assumes that:

$$C(z,t) = 0 \quad \text{for } 0 \leq t \leq z / V_z$$

It is necessary to clarify some of the other parameters used by Letey and Oddson (1972) and Oddson (1970) as they differ slightly from the traditional ones:

Vz - The velocity Vi given by the Darcy's Law and saturated hydraulic conductivity is normally used. In this case Vz is the velocity in the pore space given by:

$$V_p = V_z / \theta$$

θ is the volumetric water content and will be assumed to be 22%, which is the value established for the soil being used by Paviostathis and Jagial (1991:276).

S - The quantity of adsorbed material is normally given on a mass/mass basis. The relationship between the traditional quantity, S', and the S used in the model is as follows:

$$S = \beta S'$$

β is the bulk density. The bulk density of the soil in the study by Pavlotathis (1991) is calculated to be 2.8 g / cm^3. Thus, the product this equation is a mass of contaminant per cm^3 of soil.

K_p - The normal partitioning coefficient, K_d, is related to the one utilized in the model by:

$$K_p = K_d \beta / \theta$$

C_s - The normal solution concentration, C, is given in mass per cm^3 of solution. The C used in the model is related by the following:

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$$C_S = \theta C$$

The result is a mass of contaminant in liquid phase per volume of soil.

In the model, all of the values are calculated in the traditional units.

The liquid phase concentration at time after t_0 is as follows (Letey and Oddson, 1972:411):

$$C_i(z,t) = \frac{S(z,t)}{K_p} + C_{Li} \exp\left(\frac{-\alpha \cdot K_p \cdot z}{V_p}\right) \cdot$$

$$\exp\left[\alpha\left(\frac{t-z}{V_p}\right)\right]\left\{I_0\left[2\left(\alpha^2 K_p z \frac{t-z}{V_p^2}\right)^{\frac{1}{2}}\right] - \exp(\alpha \cdot t_0) I_0\left[2 \cdot \left[\frac{(\alpha^2 K_p z(t - \frac{z}{Vz} - t_0)}{Vz}\right]^{\frac{1}{2}}\right]\right\}$$

This model does make several assumptions which keep it from being truly predictive. One problem is the assumptions it makes about adsorption and desorption. The coefficient α is only valid if the rate of sorption is constant over time. This may not be true for TCE, and it is definitely not true for some organic chemicals. The model also assumes that sorption is entirely reversible, and this may also be a faulty assumption (Oddson and others, 1970:416). In addition, it neglects the vapor phase interactions which may be present. The current state of research is not able to describe the adsorption behavior of vapor phase TCE in soils (Peterson and others, 1988:571). The error involved in not including the vapor phase may or may not be significant because at the time the penetration is being modeled most of its pore space will be occupied by solution. The model is still a useful description of chemical behavior and provides insights into the factors that influence it.

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Exposure In the Air Phase Due to Irrigation

For modeling the air under the crop canopy, the water reaching the crop will be assumed to be deposited immediately under the crop and pond there. For the evaluation of the exposure in the air under the corn canopy, the water will be assumed to not infiltrate the soil. This will tend to overestimate the exposure that would actually take place as this makes more mass of TCE readily available. In reality, the when the TCE infiltrates the soil it would evaporate much more slowly due to sorption and limited exposure to the air.

The model used will treat the ponded TCE aqueous solution as a homogenous concentration which interfaces with the air at x = 0. The coordinate system will assume that x is positive in the vertical up direction. All of the water will be assumed to be deposited at time t = 0.

The diffusivity varies both with elevation and with time of day. Solutions to the diffusion differential equations which allow this dual variation have not been located. However, a solution which allows the diffusivity to vary over time is available. The concentration will be evaluated at individual elevations using the effective diffusivity discussed earlier. With the elevation held constant, the diffusivity varies only with time. These points can be assembled to obtain a complete concentration profile for the corn canopy. Crank (1970:12) presents a solution for a planar source. The solution is as follows:

$$C(x_1, \lambda) = \frac{C_{LI}}{2(\pi \cdot \lambda)^{\frac{1}{2}}} \exp\left[\frac{-x^2}{4 \cdot \lambda}\right]$$

The evaluated λ is substituted to allow the diffusivity to vary over time. Crank (1970) gives the variable as follows:

$$\lambda = \int_0^t K_E(\tau) d\tau$$

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One unique aspect of this physical situation is the air/water interface. There is a transfer coefficient in the liquid and gas film layer which must be included in the evaluation of K_E.

IV. Results

Air Exposure Due to Soil Gas.

The crop canopy concentrations (ppm) of TCE resulting from a flux of 12 $\mu g/m^2$-day are plotted for three different times of day in Figures 6 through 8. The quantity of a $\mu g/cm^3$ has been converted to ppm on a volume/volume basis assuming that the unit of $1\mu g/cm^3$ is equal to 2 ppm (ATSDR, 1989:33). The diffusivity values which lead to these concentrations are shown in Figure 5 for 0800 and 1200. The molecular diffusion that is dominant during the night hours is negligibly small in comparison to these values and was thus not shown. All of the graphs in this section are summarized in Table 6.
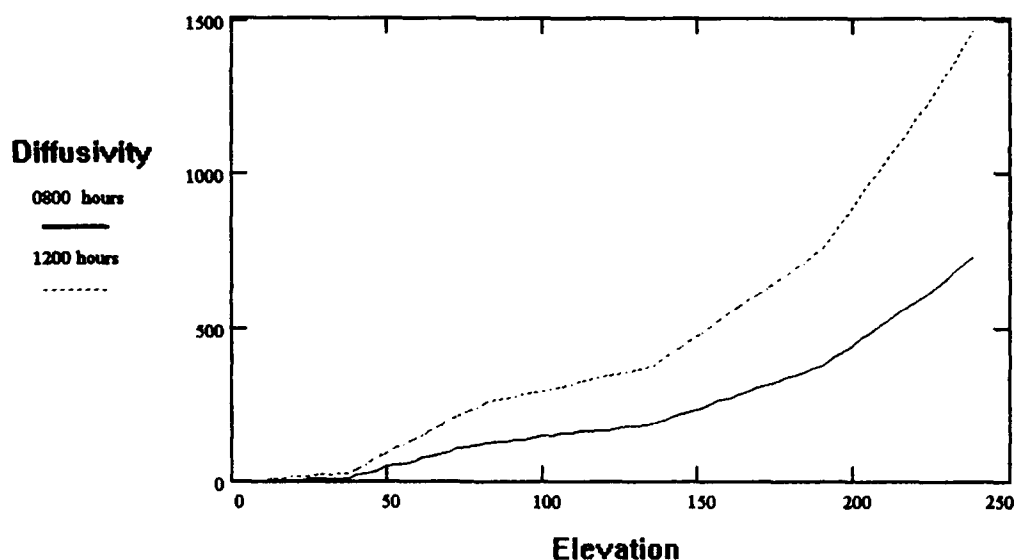

Figure 5: Diffusivity (cm/s) as a function of elevation (cm) within the crop canopy at 0800 and 1200 hours.
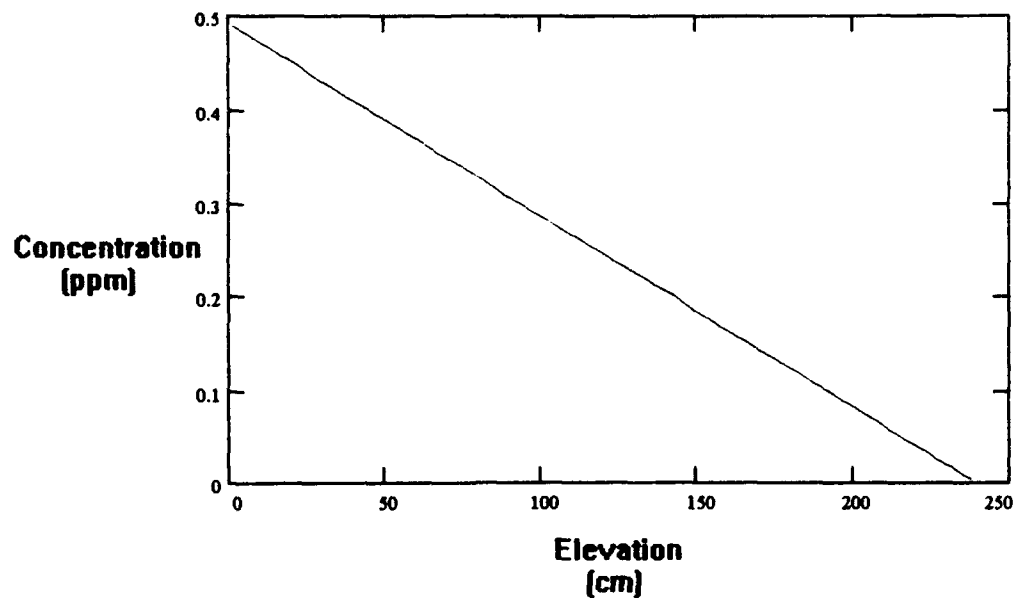
Figure 6: Concentration (ppm) of TCE at elevation (cm) within the crop canopy at 0200 hours due to a flux of 12 $\mu g/m^2$-day.
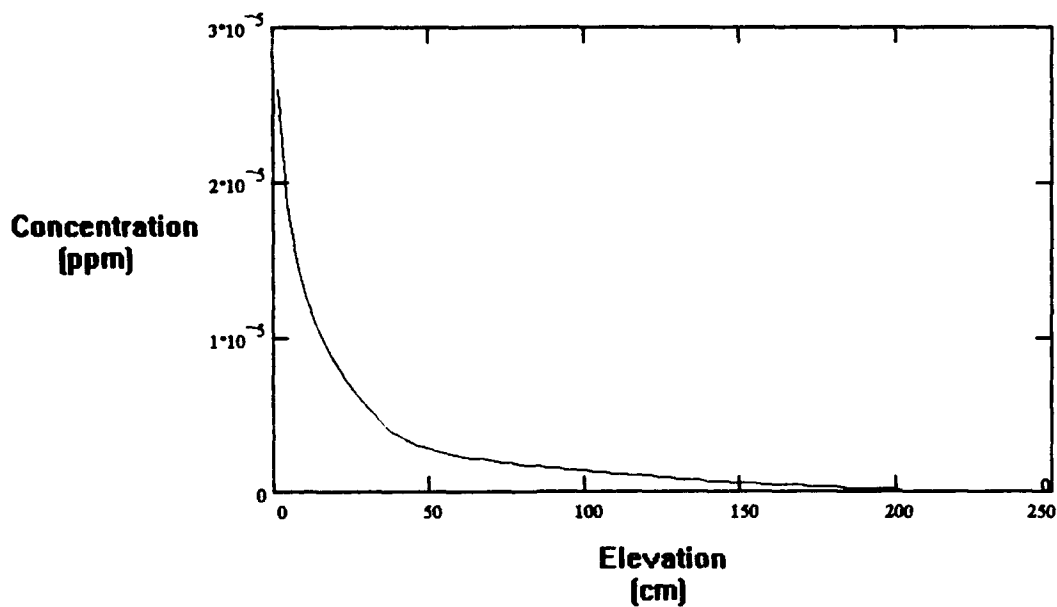
Figure 7: Concentration (ppm) of TCE at elevation (cm) within the crop canopy at 0800 hours due to a flux of 12 $\mu g/m^2$-day.

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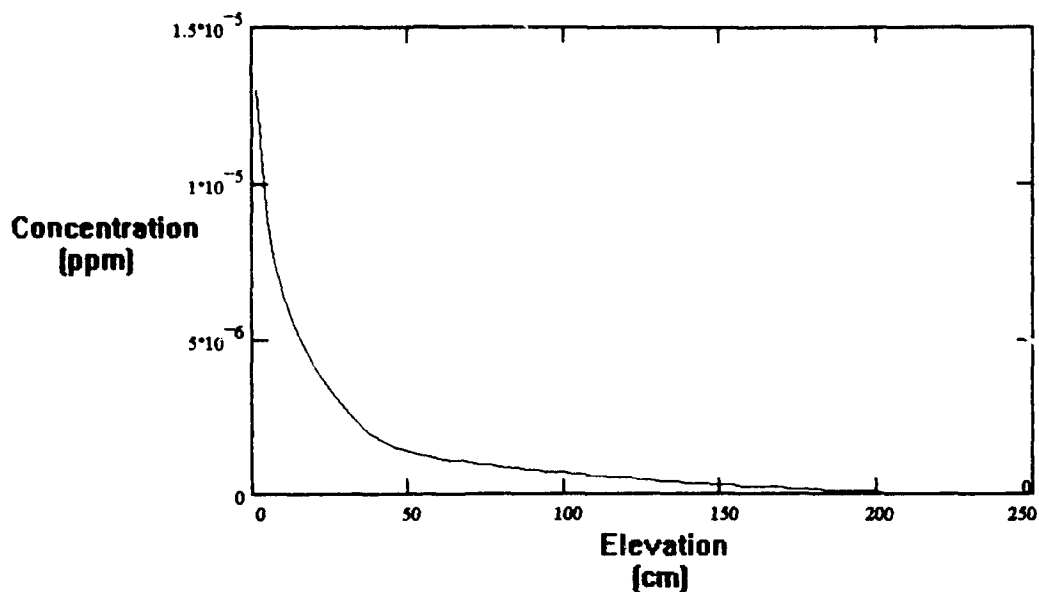
Figure 8: Concentration (ppm) of TCE at elevation (cm) within the crop canopy at 1200 hours due to a flux of 12 μg/m^2-day.

Figure	Distance	Flux Rate (μg/m^2-day)	Time of Day (hours)	Parameter Modeled
5	Elev. = 0-240 (cm)	12	0800, 1200	Diffusivity (cm/s)
6	Elev. = 0-240 (cm)	12	0200	Concentration (ppm)
7	Elev. = 0-240 (cm)	12	0800	Concentration (ppm)
8	Elev. = 0-240 (cm)	12	1200	Concentration (ppm)

Table 6: Summary of graphs used to describe soil gas activity.

<u>Losses During Transport.</u>

<u>Spray Irrigation.</u> The spray of a TCE contaminated water is modeled in Figure 9 below. The concentration arriving at the crop is shown as a function of the concentration in the original aquifer water. The TCE which is lost to the atmosphere is considered to be removed and has no potential to expose the corn crop. The concentrations are given in μg/L and therefore correspond to ppb on a mass/volume basis.
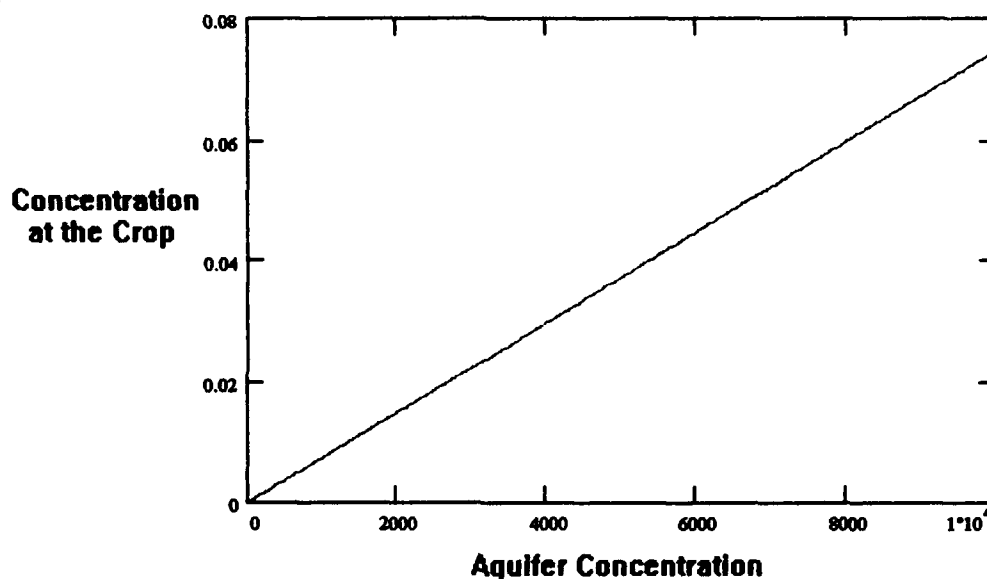
Figure 9. The concentration (μg/L) of TCE reaching the crop due to spray irrigation is shown as a function of the initial concentration of TCE in the aquifer (μg/L).

<u>Flood Irrigation.</u> The concentration of TCE in the water arriving at the corn crop during flood irrigation is modeled in Figure 10 below. The amount of TCE delivered is shown as it varies with the distance that the water has to travel to get to the crop. The model assumes that the TCE is transported in a culvert with a uniform depth of .5 m and that the initial concentration is 16 μg/L.

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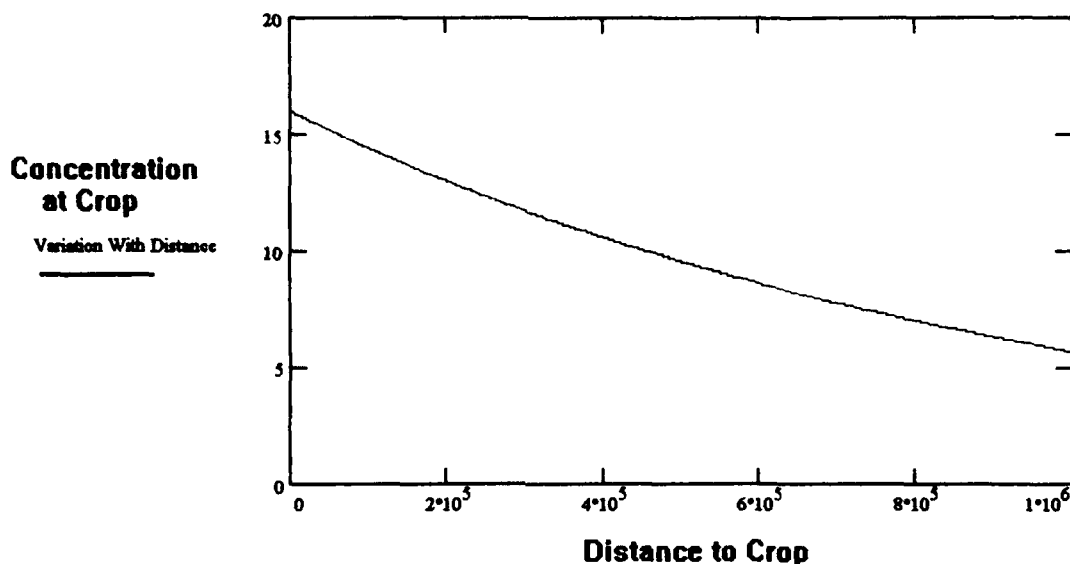
Figure 10: The concentration (μg/L) of TCE reaching the crop due to flood irrigation is shown as a function of the distance (m) the TCE travels to the field in transport.

Crop Exposure Due to Irrigation

Air Exposure. The following figures show the results for the transport of the TCE up through the crop canopy. Figures 11 through 13 model the variation of concentration with elevation and time after a 0600 irrigation. As discussed previously, the units of air concentration are ppm on a volume/volume basis.,

The concentration is next, in Figure 14, modeled at an elevation of 10 cm for an extended period after irrigation to observe the attenuation of the TCE. In Figure 15, the attenuation is observed during the extreme outlying hours. All of the graphs in this section are summarized in Table 7.

Exposure In Soil. In Figure 16, the aqueous concentration of TCE is shown as a function of the depth at the time when the water completes the infiltration into the soil. The units of liquid phase TCE are μg/L, which corresponds to roughly a ppb on a mass/mass basis. In Figure 17, the concentrations of sorbed and liquid phase TCE are shown in units of μg/cm^3. Assuming a bulk density of 2.8 g/cm^3,

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1 μg/cm³ corresponds to approximately .36 ppb on a mass/mass basis.
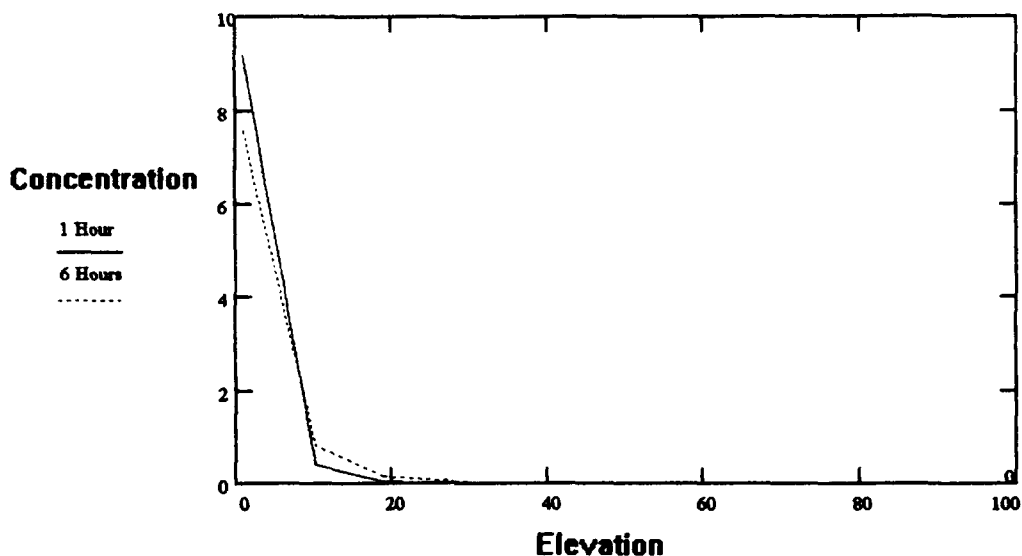
Figure 11: The concentration of TCE (ppm) is plotted as a function of the elevation within the crop canopy (cm) at a time 1 hour and 6 hours after a 0600 irrigation. The data assumes 16 μg/L concentration reaching the crop and 1.4 cm of average rainfall.
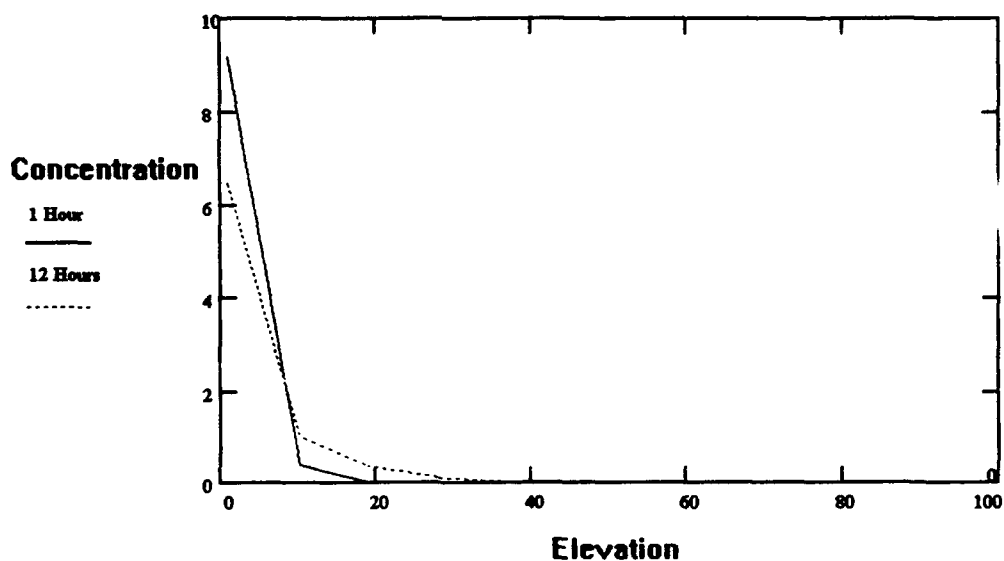
Figure 12: The concentration of TCE (ppm) is plotted as a function of the elevation within the crop canopy (cm) at a time 1 hour and 12 hours after a 0600 irrigation. The data assumes 16 μg/L concentration reaching the crop and 1.4 cm of average rainfall.
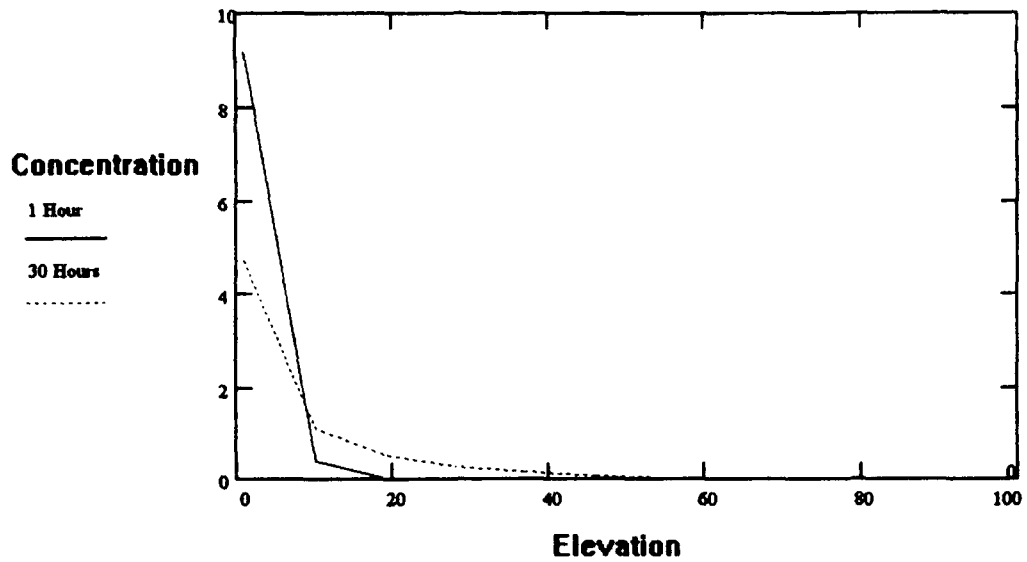
Figure 13: The concentration of TCE (ppm) is plotted as a function of the elevation within the crop canopy (cm) at a time 1 hour and 30 hours after a 0600 irrigation. The data assumes 16 µg/L concentration reaching the crop and 1.4 cm of average rainfall.
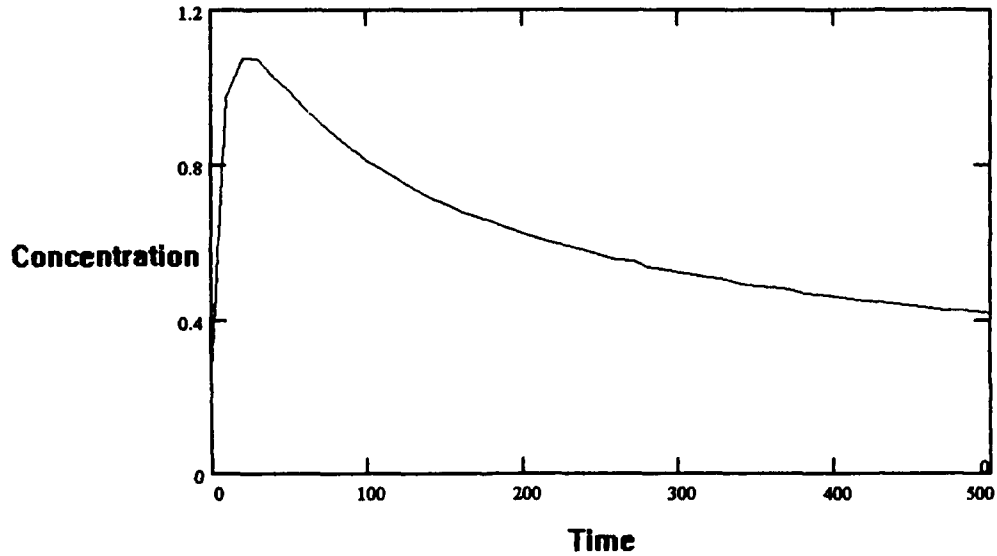
Figure 14: The concentration of TCE (ppm) at a height of 10 cm is plotted as a function of time (hours) after a 0600 irrigation. The data assumes 16 µg/L TCE reaching the crop and 1.4 cm of average rainfall.

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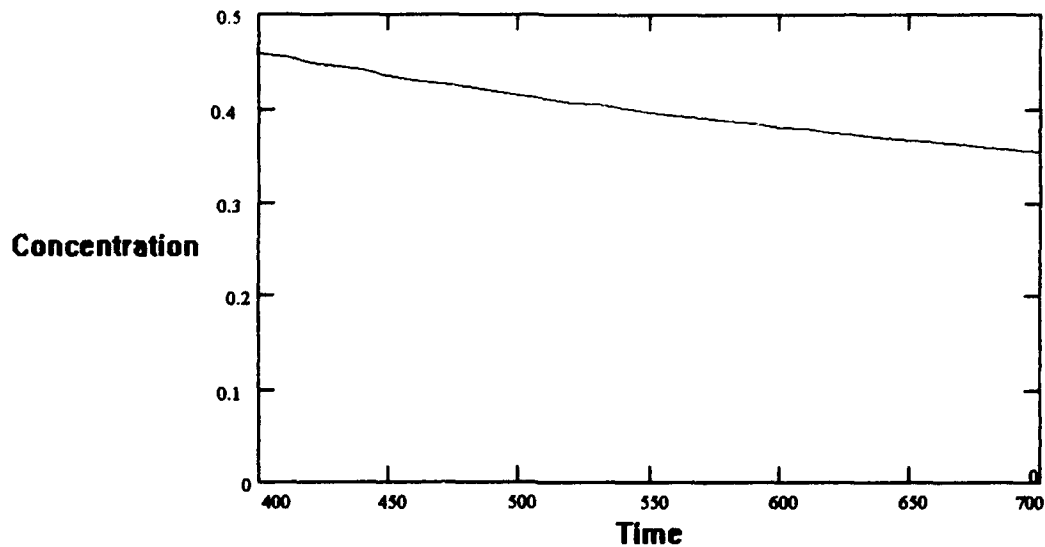
Figure 15: The concentration of TCE (ppm) at a height of 10 cm is plotted as a function of time (hours) after a 0600 irrigation. The data assumes 16 µg/L concentration reaching the crop and 1.4 cm of average rainfall.

Figure	Time After Irrigation (Hours)	Concentration in Irrigation Water (µg/L)	Elevation (cm)	Parameter Modeled
11	1,6	16	0-240	Concentration (ppm)
12	1,12	16	0-240	Concentration (ppm)
13	1,30	16	0-240	Concentration (ppm)
14	0-500	16	10	Concentration (ppm)
15	400-700	16	10	Concentration (ppm)

Table 7: Summary of graphs used to model the crop air exposure.

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The aqueous concentration of TCE is modeled as it varies with the parameters of sorption rate and sorption equilibrium. In Figure 18, K_d is held constant and the impact of a variation of α is observed. In Figure 19, α is held constant and the concentrations are observed for two different values of K_d. All of the graphs used to model the exposure in the soil phase are summarized in Table 8 below.

Affect of Rainfall. The influence of rainfall is modeled as pure water being applied after the contaminated water has completely entered the soil. Figure 20 illustrates the influence of the rainfall on the concentration profile of the liquid phase contaminant.
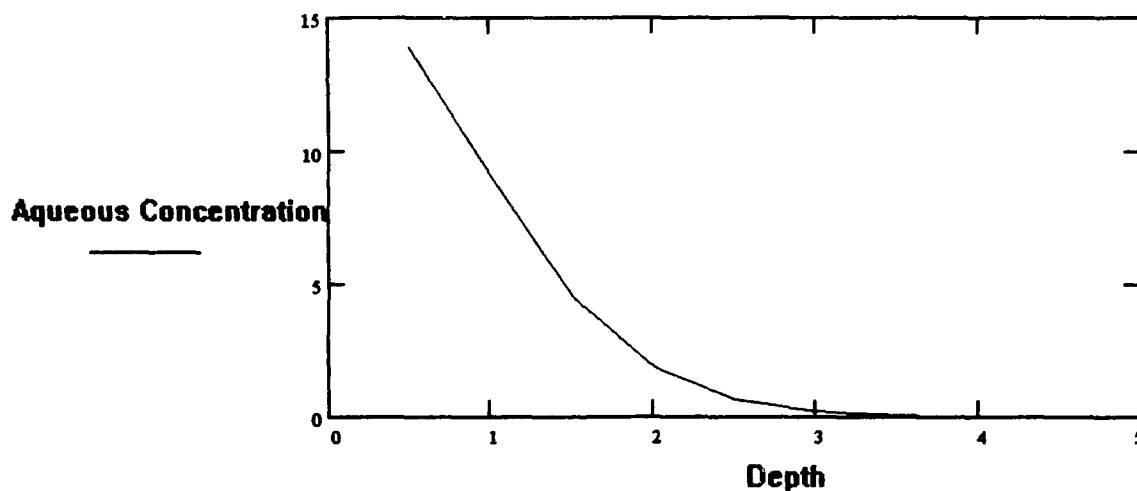
Figure 16: The concentration of TCE (μg/L) in aqueous phase in the soil is plotted as a function of depth (mm). The data assumes t = 100 sec, concentration reaching the crop is 16 μg/L, α = .05, and K_d = 11.7 ml/g.
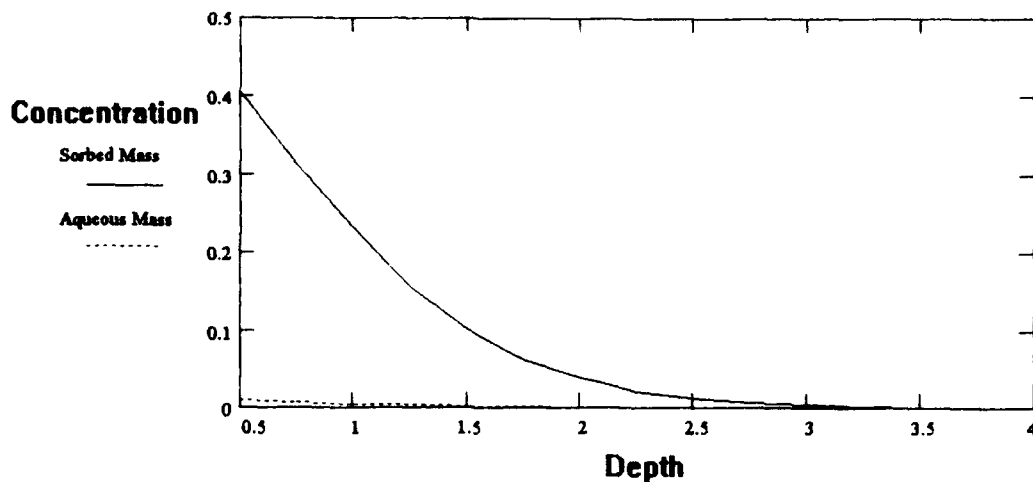
Figure 17: The mass of TCE ($\mu g/cm^3$) sorbed (solid line) and in the aqueous phase ($\mu g/cm^3$) (dashed line) is plotted as a function of depth (mm). The data assumes t = 100 sec, K_d = 11.7 ml/g, α = .05, and the concentration of TCE reaching the crop is 16 $\mu g/L$.
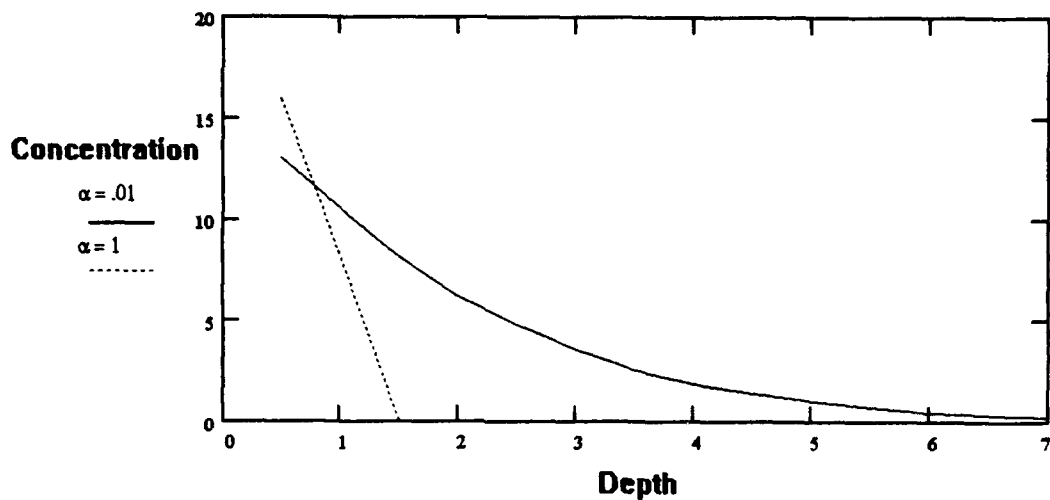
Figure 18: The concentration of TCE in aqueous phase ($\mu g / L$) at α =.01 (solid line) and the concentration of aqueous TCE ($\mu g / L$) at α =.1 (dashed line) are plotted with depth (mm). The data assumes t =100 sec and K_d= 11.7 ml/g.
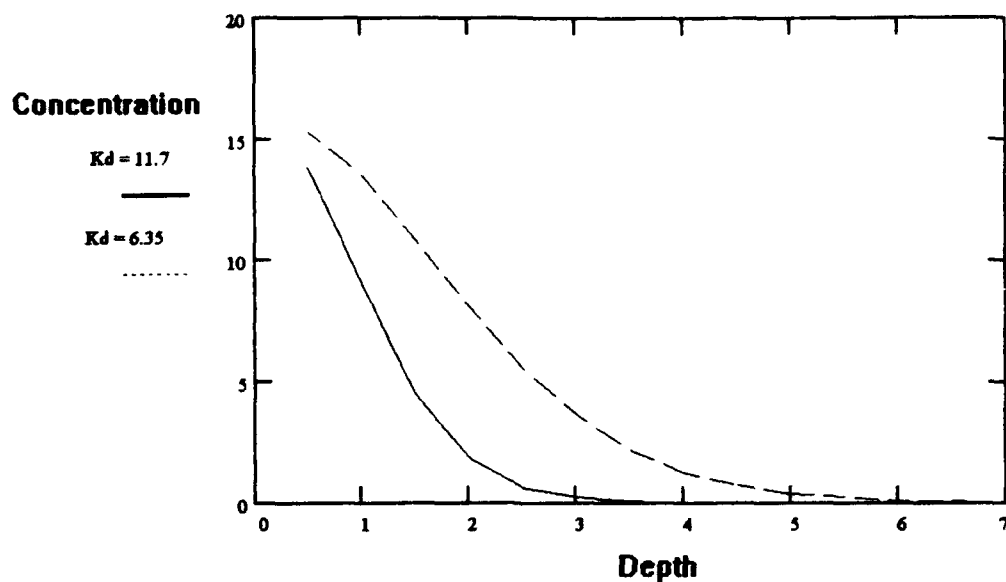
Figure 19: The concentration of TCE ($\mu g / L$) in aqueous phase at K_d = 11.7 ml/g (solid line) and at K_d = 6.35 ml/g (dashed line) are plotted as a function of depth (mm). Data assumes t =100 sec, α = .05 ml/g, and concentration reaching the crop is 16 $\mu g / L$.
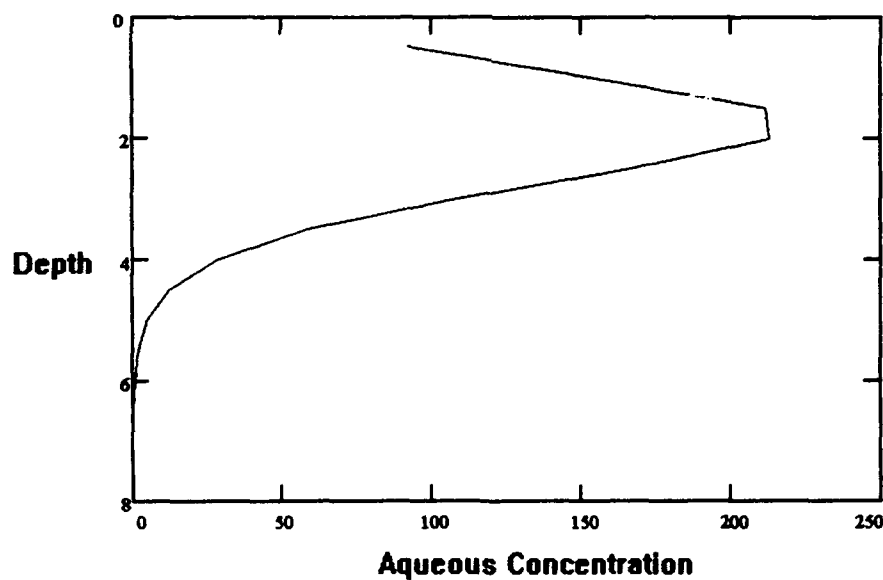
Figure 20: The concentration of TCE in the aqueous phase ($\mu g/L$) is shown as a function of depth. The data assumes t = 200 sec. K_d= 11.7 ml/g, α = .05 and the concentration of TCE reaching the crop is 16 $\mu g/L$.

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Figure	Sorption Equil. Coeff. (ml/g)	Sorption Rate (unitless)	Concentration in Water (μg/L)	Time After Irrigation (sec)	Parameter Modeled
16	11.7	.05	16	100	Aqueous Conc. (μg/L)
17	11.7	.05	16	100	Aqueous and Sorbed Conc. (μg/cm^3)
18	11.7	.01, 1	16	100	Aqueous Conc. (μg/L)
19	6.35, 11.7	.05	16	100	Aqueous Conc. (μg/L)
20	11.7	.05	16	200	Aqueous Conc. (μg/L)

Table 8: Summary of graphs used in modeling the leaching of ⸱⸱ ⸱ into the soil environment.

V. Discussion and Conclusions

Air Exposure Due to Soil Gas

The air phase exposure due to soil gas is shown in Figures 6, 7 and 8. At night the concentrations are expected to be highest due to lower diffusivity. The concentrations are all parts per trillion in magnitude. The concentrations during the more turbulent daytime hours are all more than 4 orders of magnitude less than those at night and would quite likely be undetectable. It is important to remember that this model was done with the assumption that the system had reached steady state. The actual numbers are possibly quite lower than the ones calculated here, but it is safe to say that they are not higher. The levels of TCE in the parts per trillion range, lacking significant biomagnification in the corn, are considered insignificant and the actual numbers are likely much lower than those calculated. The exposure due to soil gas is therefore considered negligible in the air phase.

Transport

Spray Irrigation. The modeling of transport of water to the crop by spray irrigation is shown in Figure 9. Based on the model used, more than 99% of the TCE can be expected to be removed from the water. While this varies significantly from the study conducted by Giardino (1992), the study by Giardino did not assume that the ambient concentration was negligible as was done in this model. The study by Giardino (1992) was examining volatilization in a shower and the assumption was therefore not appropriate. The 99% removal of TCE provides an opportunity to reduce the exposure of the corn by selection of irrigation systems.

Flood Irrigation. The losses during flood irrigation are shown in Figure 10. The volatilization using this method of irrigation is much lower and, for the numbers that would be expected reasonable in an agricultural situation, no significant loss of TCE occurs. For the losses to be significant, the distance traveled by the water to the crop has to be on the order of hundreds of kilometers.

Crop Exposure Due to Irrigation

Air Exposure. The exposure in the air phase is shown in Figures 11 through 13. The concentrations are all less than 10 ppm. These concentrations are very near concentrations which can be breathed directly without significant risk to human health (ATSDR, 1989:3). Without significant biomagnification, the exposure can be considered negligible. It is noteworthy that these concentrations are only present in the very lowest regions of the crop canopy. Figure 14 shows a profile over time for a height of 10 cm. This Figure demonstrates that, even as low as 10 cm, the concentrations do not exceed a ppm. The height of the concentration is significant because leaves, where transpiration takes place, are the most likely place for uptake of TCE (Bleckmann, 1994). The higher concentrations are much less likely to be available for uptake. In addition, the assumption of ponding is conservative and the leaching of contaminated water would limit the contamination to levels below the ones found here.

Soil Exposure. The aqueous TCE concentration is shown in Figure 16. The level of contamination below 2 mm is shown to be in the ppb range. The majority of the mass of TCE is retained in the top 2 mm of soil. These results are consistent with those of Letey and Oddson (1972). At these levels of soil penetration it is doubtful that the roots would be exposed. Figure 17 compares the sorbed mass to the aqueous mass. The importance of this is that, as mentioned previously, the sorbed

mass is not available for uptake by the plant. The model demonstrates that nearly all of the mass of the TCE is sorbed by the soil and therefore not going to be taken up by the plant.

The impact of the sorption parameters is modeled in Figures 18 and 19. If either the rate of sorption or the sorption equilibrium coefficient decreases significantly the depth of penetration by the aqueous TCE increases. If it is not sorbed to the soil rapidly or if the soil capacity to so᎑   ᎑᎑ is low, the TCE continues to flow into the lower levels of the soil where the roots may be exposed. In a moist soil environment, the sorption is mostly by way of the organic matter in the soil. The organic matter in the soil, therefore, plays an important role in determining K_d and, hence, the depth of penetration by the TCE. Very little is known about the sorption rate coefficient for TCE. In order to get a good idea of the actual penetration more research will have to be conducted to better define this parameter for TCE. From the results of the model, it can be concluded that the properties of the soil are important in determining the likely exposure to TCE.

Figure 20 shows the impact of rain on the TCE. The TCE is pushed down through the soil in a wave, and the more rain takes place the more TCE reaches the area of the roots. The rain therefore increases the likelihood of the uptake of the TCE by the plant.

The rainfall amounts modeled in Figure 20 were approximately twice the average monthly rainfall at Hill AFB. Based on the model in Figure 24, a corn crop outside Hill AFB could reasonably expect to have 200 ppb or less of aqueous TCE at a depth of less than 4 mm. While 200 ppb may be a potentially risky amount of TCE if it is available for uptake by the plant, the depth of penetration is still minimal and will mitigate the effects. It is important to note the interesting result that irrigation with 16 ppb aqueous solution of TCE resulted in a contamination at the

200 ppb level. This may be due to the sorption properties of the soil retarding the penetration of the TCE relative to the penetration of the water.

Conclusions

Based on a review of the literature, a methodology, consisting primarily of a series of models, was developed for evaluation of the exposure pathways for TCE between a contaminated aquifer and a food crop. Using information gathered about the climate and environmental conditions near Hill AFB, the model was used to examine the potential for a problem at that location due to an existing TCE contamination. The methodology did provide significant information about the potential for a risk to human health. The most important contributions are as follows:

- the air exposure due to soil gas is negligible
- the method of irrigation is an important factor in the exposure
- the air exposure due to irrigation is negligible and much of the resulting vapor phase TCE is unavailable for uptake by the plant
- the soil exposure is mitigated by the lack of penetration of the TCE and the potential for exposure is influenced by the properties of the soil
- rainfall assists the penetration of the TCE toward the roots

The methodology does, therefore, contribute useful information about factors influencing risk to human health. With the types of information that are provided, the risk analysis and prevention at a contaminated site can be guided much more effectively.

Bibliography

Agency for Toxic Substances and Disease Registry. Toxicological Profile for Trichloroethylene. (October 1989).

Agency for Toxic Substances and Disease Registry. Public Health Assessment Guidance Manual. Chelsea, MI: Lewis Publishers (1992).

Agency for Toxic Substances and Disease Registry. Public Health Assessment for McClellan Air Force Base (CERCLIS NO. CA4570024337) (March 22, 1994).

Altwicker, E. B. and others."Absorption of Gases Into Drops," AIChe Journal, 34: 329-332 (1988).

American Conferene of Governmental Industrial Hygienists, Inc. Documentation of the Threshold Limit Values and Biological Exposure Indices 5th ed. 595 (1986).

Barrio-Lage, Gladys, and others. "Kinetics of the Depletion of Trichloroethene," Environmental Science and Technology, 21: 366-369 (1987).

Bishop, P. K. and others. "Soil gas surveying of chlorinated solvents in relation to groundwater pollution studies," Quarterly Journal of Enginering Geology, 23: 255-265(1990).

Bleckmann, Charles. Assistant Professor of Engineering and Environmental Management, Air Force Institute of Technology, Wright Patterson AFB, Ohio. Personal Correspondence. 8 Aug. 1994.

Bodner, George M. and Harry L. Pardue. Chemistry: An Experimental Science. New York: John Wiley and Sons, 1989.

Boesten, J. J. T. I. "Bioavailability of Organic Chemicals in Soil Related to Their Concentration in the Liquid Phase: a Review," The Science of the Total Environment, (Supplement): 397-407 (1993).

Bourg, Alain C., and others. "A review of the attenuation of trichloroethylene in soils and aquifers," Quarterly Journal of Engineering Geology, 25: 359-370 (1992).

Callahan, Michael A. and others. Water-Related Environmental Fate of 124 Priority Pollutants. Vol II. Halogenated Aliphatic EPA-44014-79-029B, Springfield, VA: USEPA, 1979.

Chiou, Cary T. and others. "Evaporation of Solutes from Water," Environment International, 3: 231-236 (1979).

Chiou, G. T. and others. "Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanism and Capacity," Environmental Science and Technology, 19: 1196-1200 (1985).

Chiou, Gary T. "Roles of Organic Matter, Minerals, and Moisture in Sorption of Nonionic Compounds and Pesticides by Soil," in Humic Substances in Soil and Crop Sciences: Selected Readings. Madison, WI: American Society of Agronomy and Soil Science Society of America, 111-156 (1990).

Couliette, David L., Major, USAF. Assistant Professor of Mathematics and Statistics, Air Force Institute of Technology, Wright Patterson AFB, Ohio. Personal Correspondence. 8 July 1994.

Crank, J. C. Mathematics of Diffusion. Oxford University Press: London, 1970.

Dilling, Wendell, and others. " Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethytlene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions," Environmental Science and Technology, 9(9): 833-837 (1975).

Dilling, Wendell L. "Interphase Transfer Processes. II. Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and Propylenes from Dilute Aqueous Solutions. Comparisons with Theoretical Predictions," Environmental Science and Technology, 11(4): 405-409 (1977).

Domenico, Patrick A. and Franklin W. Schwartz. Physical and Chemical Hydrogeology. New York: John Wiley and Sons, 1990.

Doorenbos, J. and W. O. Pruitt. Guidelines for Predicting Crop Water Requirements. Rome: Food and Agriculture Organization of the United Nations, 1977.

Fetter, C. W. Applied Hydrology. McMillan Publishing Company: New York, 1988.

Giardino, Nicholas J., and others. "Modeling Volatilization of Trichloroethylene from a Domestic Shower Spray: the Role of Drop-Size Distribution," Environmental Science and Technology, 26(8): 1602-1607 (1992).

Gillham, R. W. and P. S. C. Rao. "Transport, Distribution and Fate of Volatile Organic Compounds in Ground Water," in Significance and Treatment of Volatile Organic Compouns in Water Supplies. Chelsea, MI:Lewis Publishers, 1990.

Godish, Thad. Air Quality. Chelsea, MI: Lewis Publishers, Inc., 1991.

Gross, Randy L., and Stephen G. Termaath. "Packed Tower Aeration Strips Trichloroethylene from Groundwater," Environmental Progresss, 4(2): 119-125 (May 85).

Hauser, Thomas R. Distinguished Visiting Professor, Air Force Institute of Technology, Wright Patterson AFB, Ohio. Personal Correspondence. 8 July 1994.

Hartman, Hudson T., Anton M. Kofranek, Vincent E. Rubatzky, and William J. Flocker. Plant Science: Growth, Development, and Utilization of Cultivated Plants (Second Edition). Englewood Cliffs, New Jersey: Prentice-Hall, Inc., 1988.

Ho, James S.-Y., "Effect of Sampling Variables on Recovery of Volatile Organics in Water," Journal of the American Water Works Association 75: 583-586 (1983).

International Station Meteorological Climate Summary, Ver 2.0 (Jun 92).

Jury, W. A. "Chemical Movement Through Soil," in Vadose Zone Modeling of Organic Pollutants. Chelsea, MI: Lewis Publishers Inc., 1986.

Jury, W. A. "Volatilization From Soil," in Vadose Zone Modeling of Organic Pollutants. Chelsea, MI: Lewis Publishers Inc., 1986b.

Kimbrough, Renate D., and others. "Trichloroethylene: an Update," Journal Toxicology & Environmental Health, 15: 369-384 (1985).

Kuethe, Arnold M. and Chuen-Yen Chow. Foundations of Aerodynamics: Bases of Aerodynamic Design, (Fourth Edition). New York: John Wiley and Sons, 1986.

Lappala, Eric G. and Glen M. Thompson. "Detection of Groundwater contamination by shallow soil gas sampling in the vadose zone," Proceedings of the NWWA/EPA conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone. Las Vegas, Nevada: National Water Well Association, 659-679 (1983).

Letey J. and J. K. Oddson. "Mass Transfer," in Organic Chemicals in the Soil Environment. New York: Marcel Dekker Inc.,1972.

Liss, P. S. and others. "Flux of Gases across the Air-Sea Interface," Nature, 27: 181-184 (1974).

Mackay, Donald and Aaron Wolkoff. "Rate of Evaporation of Low-Solubillity Contaminants from Water Bodies to Atmosphere," Environmental Science and Technology, 7: 611-614 (1973).

Mackay, D. and P. J. Leinonen. "Rate of Evaporation of Low-Solubiliity Contaminants from Water bodies to Atmosphere," Environmental Science and Technology, 9: 1178-1180 (1975).

Marrin, D. L. and G. M. Thompson. "Remote Detection of Volatile Organic Contaminants in Groundwater Via Shallow Soil Gas Sampling," Proceedings of the Petroleum Hydorcarbons and Organic Chemicals in Groundwater Conference. Houston, Texas: National Water Well Association, 172-186 (1984).

Marrin, Donn L. and Glenn M. Thompson. "Gaseous Behavior of TCE Overlying a Contaminated Aquifer," Ground Water, 25(1): 21-27 (January-February 1987).

Marrin, Donn L. and Henry B. Kerfoot. "Soil-Gas Surveying Techniques," Environmental Science & Technology, 22: 740-745 (1988).

Marrin, Donn L. "Soil-Gas Sampling and Misinterpretation," Ground Water Monitoring Review, 8: 51-54 (Spring 1988).

Masters, Gilbert M. Introduction to Environmental Engineering and Science. Englewood Cliffs, NJ: Prentice Hall. 1992.

McKone, Thomas E. and John P. Knezovich. "The Transfer of Trichloroethylene (TCE) from a Shower to Indoor Air: Experimental Measurements and Their Implications," Air & Waste Management Association Journal, 41(6): 832-838 (1991).

Morrison, Robert T. and Robert Neilson Boyd. Organic Chemistry. Englewood Cliffs, NJ: Prentice Hall, 1992.

Oddson, J. K., and others. "Predicted Distribution of Organic Chemicals in Solution and Adsorbed as a Function of Position and Time for Various Chemical and Physical Properties," Soil Science Society of America Proceedings, 34: 412-417 (1970).

Parmele, L. H. and others. "Micrometeorological Measurement of Pesticide Vapor Flux From Bare Soil and Corn Under Field Conditions," Water, Soil Air Pollution, 1: 433-451 (1972).

Paviostathis, Spyros G. and Kendrick Jagial. "Desorptive Behavior of Trichloroethylene in Contaminated Soil," Environmental Science and Technology 25(2): 274-279 (1991).

Pearsall, Kenneth A. and others. "Effects of Selected Sampling Equipment and Procedures on the Concentrations of Trichloroethylene and Related Compounds in Ground Water Samples," Ground Water Monitoring Review, 7(2): 64-73 (1987).

Peterson, Michele S. and others. "Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in an Unsaturated Aquifer System," Environmental Science and Technology, 22(5): 571-578 (1988).

Pettyjohn, W. A., and others. "Sampling Ground Water for Organic Contaminants," Ground Water, 19(2): 180-189 (1981).

Radian Corporation. Remedial Investigation Report: Operable Unit 5, Hill Air Force Base, Utah, USACE/USAF Draft, Volume 1--Text. USAF Contract No. F42650-92-D0007. Austin, TX: Radian Corporation, January 1994.

Ritzi, Robert W.. Class Lecture, ENVR 640, Groundwater Hydrology and Contaminant Transport. School of Engineering, Air Force Institute of Technology, Wright-Patterson AFB OH, Oct 1993.

Runyon, Thomas A. and Glenn M. Thompson. "Soil Gas Investigations for Volatile Subsurface Contaminants: Case Studies in Kansas, USA," Environment Canada 4th Chemical Spills Technical Symposium, Toronto. 287-293 (1987).

Ryan, J. A., and others. "Plant Uptake of Non-Ionic Organic Chemicals From Soils," Chemosphere, 17(122): 2299-2323. 1988

Serway, Raymond A. Physics for Scientists and Engineers, (Second Edition). Philadelphia: Saunders College Publishing, 1986.

Spencer, William F. and others. "Behavior of Organic Chemicals at Soil, Air, Water Interfaces as Related to Predicting the Transport and Volatilization of Organic Pollutants," Environmental Toxicology and Chemistry, 1: 17-26 (1982).

Spencer, William and others."Volatilization of Organic Chemicals from Soil as Related to Their Henry's Law Constants," Journal Environmental Quality, 17(3): 504-509 (1988).

Taylor, Alan W. and others. "Volatization of Dieldrin and Heptachlor from a Maize Field," Journal of Agricultural Food Chemistry, 24(3): 625-632 (May-June 1976).

United States Environmental Protection Agency. Estimating Potential for Ocurrence of DNAPL at Superfund Sites. Publication: 9355.4-07FS, January 1992.

U.S. Environmental Protection Agency. Health Assessment Document for Trichloroethylene. EPA/600/8.82/006F July 1985.

U.S. Environmental Protection Agency. Exposure Factors Handbook. EPA/600/8.89/043 1989

Weast, Robert C.(editor). Handbook of Chemistry and Physics, (65th Edition). Boca Raton, FL: CRC Press, Inc.,1985.

Appendix 1: Distribution coefficient data points (Parmele and others, 1972:446)

Elevation in Crop Canopy, x (cm)	Distribution Coefficient, ψ (unitless)
240	1.0
227	.85
189	.50
135	.25
81	.17
37	.02
0	0

Appendix 2: Vapor transfer coefficients at the top of the corn (Parmele and others, 1972:444)

Time	Vertical Vapor Diffusivity at 240 cm (in cm^2/sec)
0000	0
0200	0
0400	0
0600	300
0800	750
1000	1500
1200	1500
1400	1500
1600	700
1800	500
2000	250
2200	0

Appendix 3: Parameters and variables used in the literature review

Variable	Symbol	Units
Octanol/Water Partition Coefficient	K_{ow}	Unitless
Octanol/Carbon Partition Coefficient	K_{oc}	Unitless
Vapor Pressure	None	mm Hg
Aqueous Solubility	None	g/L
Henry's Law Coefficient	K_H	$Pa\ m^3/mol$ or
Adsorption Equilibrium Constant for TCE	K_d	mL/g
Molecular Weight TCE	M	g/mol
Concentration	C	$\mu g\ /\ L$
Diffusion Coefficient	D	cm^2/sec
Flux	F, J_v	$\mu g\ /\ cm^2$
Porosity	ϕ	Unitless
Volume of Soil	V	cm^3
Volume of Voids	V_v	cm^3
Tortuosity Factor	η	
Sorbed Mass of Contaminant	S	μg
Absorption Rate	α	Unitless

Appendix 4: Parameters and variables used in the model

Parameter or Variable	Symbol	Units
Diffusivity Distributing Coefficient	ψ	Unitless
Elevation Within Corn Canopy	x	cm
Diffusivity at Top of Corn Crop	K_z	cm^2/sec
time	t	sec
Diffusion Coefficient at Elevation within Canopy	KA	cm^2/sec
Effective Diffusivity	KE	cm^2/sec
Effectivity Diffusivity at Top of Corn	K_T	cm^2/sec
Height of Corn	X	cm
Concentration of TCE Reaching Surface Under Crop	C_{L1}	$\mu g / L$
Soil Gas Flux	F	$\mu g / cm^2$
Concentration at Ground Surface	C_{sg0}	$\mu g / cm^2$
Average Temperature	T	°C
Average Rainfall	Pe	cm

Crop Evapotranspiration	ET_o	mm / day
Leaching Requirement	LR	unitless
Efficiency of Irrigation System	EP	%
Ground Water Contribution	Ge	mm/day
Water Stored In Soil	Wb	mm/day
Empirical Correction Factor	σ	unitless
mean percentage of annual daytime hours	p	%
Uncorrected Evapotranspiration coefficient	f	mm / day
Crop Evapotranspiration	ETcrop	mm / day
Crop Evapotranspiration Coefficient	Kc	unitless
Net Irrigation Requirement	In	mm / month
Total Volume of Irrigation Water Applied	V_i	mm / month
Weekly Irrigation Volume	Vper	mm / week

Liquid Phase Mass Transfer Coefficient	K_L	cm / s
Velocity of Water Drop	V_d	cm / s
Viscosity of Water	μ_d	$N \cdot sec / m^2$
Viscosity of Air	μ_a	$N \cdot sec / m^2$
Concentration of TCE in Aquifer Water	C_0	$\mu g / L$
Drop Diameter	d	cm
Residence Time of Drop in Air	t_d	sec
Initial Trajectory Angle of Spray	a	degrees
Mass Transfer Coefficient From Water	k	cm / sec
Molecular Weight of TCE	M	g / mole
Air Flow Coefficient	β	unitless
Liquid Turbulence Coefficient	α	unitless
Universal Gas Constant	R	J / mole °K
Velocity of the Water in the Culvert	V_w	cm/s

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Distance From Well to Crop	l	meters
Uniform Depth of Culvert	L	meters
Conductivity	K	cm / sec
Porosity	n_e	unitless
Initial Depth of Water Applied	V_i	cm
Time for Complete Infiltration	t_0	sec
Velocity of Infiltrating Water	V_z	cm / sec
Depth into the Ground	z	cm
Sorbed Mass	S	$\mu g / cm^3$
Sorbed Mass	S'	$\mu g / g$
Concentration of TCE in Solution	C_s	$\mu g / L$
Soil Volumetric Water Content	θ	%
Soil Bulk Density	β	$\mu g / cm^3$

Appendix 5: Mathcad 4.0 code used to represent soil gas exposure

The following enters the soil gas levels from the analogous California site into a vector so that the root exposure due to soil gas can be shown

$i = 0, 1 .. 4$

$$zsg = \begin{bmatrix} 0 \\ -2 \\ -3.5 \\ -11 \\ -14 \\ -20 \\ -26 \end{bmatrix} \qquad csg = \begin{bmatrix} .001 \\ .003 \\ .01 \\ .6 \\ 2 \\ 3 \\ 16 \end{bmatrix}$$

The concentrations are in ppb. The depths are in feet and converted to meters.

$Depth_i = .305 \cdot zsg_i$

The following Mathcad 4.0 template models the concentration levels within the crop canopy at any given elevation and time due to a given soil gas flux.

$$\chi := \begin{bmatrix} 0 \\ 37 \\ 81 \\ 135 \\ 189 \\ 227 \\ 240 \end{bmatrix} \qquad \psi := \begin{bmatrix} 0 \\ .02 \\ .17 \\ .25 \\ .5 \\ .85 \\ 1.0 \end{bmatrix}$$

The actual data points from Parmele (1972) and the corresponding elevation within the corn canopy are entered into two vectors.

$\psi(x) := linterp(\chi, \psi, x)$

A linear interpolation is used to generate a distribution coefficient which is a continuous function of height.

$$K := \begin{bmatrix} 0 \\ 0 \\ 0 \\ 300 \\ 750 \\ 1500 \\ 1500 \\ 1500 \\ 700 \\ 500 \\ 250 \\ 0 \end{bmatrix} \qquad \varepsilon := \begin{bmatrix} 0 \\ 0200 \\ 0400 \\ 0600 \\ 0800 \\ 1000 \\ 1200 \\ 1400 \\ 1600 \\ 1800 \\ 2000 \\ 2200 \end{bmatrix}$$

The water vapor diffusivity at the top of the corn as adapted from Parmele (1972) is entered into a vector with another vector corresponding to the time of day for the data point.

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$K(t) := \text{linterp}(\varepsilon, K, t)$

Linear interpolation is used to generate diffusivities which are a continuous function of time.

$F := .0012$

The assumed flux is entered in ug/day per square centimeter.

$x := 1, 4 .. 240$

The variable x gives the elevation in 1cm increments, up to 240 cm.

$\Delta x := 1$

The increments of x are 1 cm in width.

$KA(x, t) := \text{if}(K(t) \cdot \psi(x) > 0, K(t) \cdot \psi(x), .001356)$

K(x,t) generates a diffusivity in cm2/sec. If the diffusivity from Parmele is zero, the molecular diffusion coefficient for TCE is returned. The equivalent diffusivity is then calculated by evaluating the contributions of the individual layers.

$$KE(x, t) := \frac{x}{\displaystyle\sum_{i=1}^{x} \frac{\Delta x}{KA(i, t)}}$$

$$Csg0(t) := \frac{F \cdot \frac{1}{24} \cdot \frac{1}{60} \cdot \frac{1}{60} \cdot 240}{KE(240, t)}$$

The concentration at the surface is calculated in ug/cm3.

$$Csg(x, t) := Csg0(t) - \frac{F \cdot \frac{1}{24} \cdot \frac{1}{60} \cdot \frac{1}{60} \cdot x}{KE(x, t)}$$

The concentration at any given elevation at any given time is calculated.

The following portion of the templet evaluates the concentration at a given elevation over a 24hr period or due to a range of soil gas fluxes.

$F := 0, 10 .. 100$
$t := 0, 0100 .. 2400$

The elevation, x, must be specified in cm. The range of flux must be specified in ug/day per square cm.

$$CsgF0(F, t) := \frac{F \cdot \frac{1}{24} \cdot \frac{1}{60} \cdot \frac{1}{60} \cdot 240}{KE(240, t)}$$

The concentration at the surface is calculated in ug/cm3.

The following portion of the templet evaluates the concentration at a given elevation over a 24hr period or due to a range of soil gas fluxes.

$F := 0, 10 .. 100$
$t := 0, 0100 .. 2400$

The elevation, x, must be specified in cm. The range of flux must be specified in ug/day per square cm.

$$CsgF0(F, t) := \frac{F \cdot \frac{1}{24} \cdot \frac{1}{60} \cdot \frac{1}{60} \cdot 240}{KE(240, t)}$$

The concentration at the surface is calculated in ug/cm3.

$$CsgF(F, t, x) := CsgF0(F, t) - \frac{F \cdot \frac{1}{24} \cdot \frac{1}{60} \cdot \frac{1}{60} \cdot x}{KE(x, t)}$$

The concentration at any given elevation at any given time is calculated.

Appendix 6: Mathcad 4.0 code used to model transport and irrigation volume

The following models the concentration of TCE reaching the crop from spray irrigation.

$g := 980 \quad a := 30 \quad Vd := 507 \quad d := .25$

$C0 := 0, 10 .. 10000 \qquad d := 0, 1000 .. 1000000$

The assumed values for the initial trajectory, a, the acceleration due to gravity, g (cm/s2), the drop diameter, d, and the assumed velocity.

$$td := \frac{Vd \cdot \sin\left[a \cdot \left(\frac{2 \cdot \pi}{360}\right)\right]}{g} \qquad td = 0.259$$

The residence time of the drops in air is calculated.

$\mu w := 1.0 \cdot 10^{-3} \qquad \mu a := 1.78 \cdot 10^{5}$

The viscosities of water and air are given in kg/m-s.

$$KL := \frac{.00375 \cdot Vd}{1 + \left(\dfrac{\mu w}{\mu a}\right)}$$

The mass transfer coefficient for the drops is calculated.

$$CSpr(C0) := C0 \cdot \exp\left[-KL \cdot \left(\frac{6}{d}\right) \cdot td\right]$$

The concentration of TCE in the irrigation water when it reaches the crop is calculated in the units of the aquifer contamination.

The following models the concentration of TCE reaching the crop due to flood irrigation.

$M := 130 \qquad \alpha := .9$

$\beta := 1.83 \cdot 10^{-5} \qquad KH := 1.07 \cdot 10^{5}$

$T := 24.4 \qquad R := 8.13$

$$Kexch := \alpha \cdot \beta \cdot KH \cdot \left[\frac{M \cdot \dfrac{1}{1000}}{2 \cdot \pi \cdot R \cdot 100^{2} \cdot (T + 273.16)}\right]^{\frac{1}{2}}$$

The exchange constant is evaluated.

$Vw := 1 \qquad L := .5$

The velocity of water flow in the culvert (m/s) and depth of the culvert (m) are given.

$$CF(C0, d) := C0 \cdot \exp\left(-\frac{Kexch \cdot d}{.5 \cdot 100 \cdot Vw}\right)$$

The exchange constant is used to model an exponential decay of the concentration of TCE in the water.

The following calculates the water required per weekly irrigation as a function of the average rainfall.

$p := .33 \qquad T := 24.4 \qquad Kc := 1.05$

$LR := .149$

The average daily fraction of daytime hours, leaching requirement, crop coefficient, and average temperature in July (degrees C) are given.

$f := p \cdot (.46 \cdot T + 8)$

The variable f is used to find the crop evapotranspiration, ETo, from the Tabulated data (Doorenbos, 1977:fig 1)

From the tabulated data: $Ge := 0 \quad Wb := 0 \quad Ep := 1$

$ETo := 8$

$ETcrop := Kc \cdot ETo$ The crop water requirement is calculated.

$In(Pe) := 30 \cdot ETcrop - (Pe + Ge + Wb)$ The net irrigation requirement is calculated as a function of the average rainfall. The groundwater contribution, Ge, and the water initially stored in the soil have been set to zero.

$Pe := 0, 1 .. 100$

$V(Pe) := \dfrac{1}{Ep} \cdot \dfrac{In(Pe)}{1 - LR}$ The monthly volume of water required is calculated. The irrigation system efficiency, EP, is assumed to be 100% and the leaching requirement has been set to

$Vper(Pe) := \dfrac{V(Pe)}{4}$ The depth in mm of a weekly irrigation event is calculated.

Appendix 7: Mathcad 4.0 code modeling the soil and air exposure due to irrigation

The following Mathcad 4.0 template models the exposure due to spray irrigation.

$$\chi = \begin{bmatrix} 0 \\ 37 \\ 81 \\ 135 \\ 189 \\ 227 \\ 240 \end{bmatrix} \quad \psi = \begin{bmatrix} 0 \\ .02 \\ .17 \\ .25 \\ .5 \\ .85 \\ 1.0 \end{bmatrix} \qquad K = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 300 \\ 750 \\ 1500 \\ 1500 \\ 1500 \\ 700 \\ 500 \\ 250 \\ 0 \\ 0 \end{bmatrix} \quad \varepsilon = \begin{bmatrix} 0 \\ 02 \\ 04 \\ 06 \\ 08 \\ 10 \\ 12 \\ 14 \\ 16 \\ 18 \\ 20 \\ 22 \\ 24 \end{bmatrix}$$

$\psi(x) = \text{linterp}(\chi, \psi, x)$

The actual data points from Parmele (1972) and the corresponding elevation within the corn canopy are entered into two vectors.

A linear interpolation is used to generate a distribution coefficient which is a continuous function of height.

The water vapor diffusivity at the top of the corn as adapted from Parmele (1972) is entered into a vector with another vector corresponding to the time of day for the data point.

$K(t) := \text{linterp}(\varepsilon, K, t)$ — Linear interpolation is used to generate diffusivities which are a continuous function of time.

$t := 1, 10 .. 40$ — Time is entered in hours for use in exponential decay.

$x := 1, 4 .. 240$ — The variable x gives the elevation in 1 cm increments, up to 240 cm.

$\Delta x := 1$ — The increments of x are 1 cm in width.

The following calculates the water required per weekly irrigation as a function of the average rainfall.

$p := .33 \quad T := 24.4 \quad Kc := 1.05$
$LR := .149$

The average daily fraction of daytime hours, leaching requirement, crop coefficient, and average temperature in July (degrees C) are given.

$f := p \cdot (.46 \cdot T + 8)$

The variable f is used to find the crop evapotranspiration, ETo, from the Tabulated data (Doorenbos, 1977:fig 1)

From the tabulated data: $\quad Ge := 0 \quad Wb := 0 \quad Ep := 1$
$ETo := 8$

$ETcrop := Kc \cdot ETo$ — The crop water requirement is calculated.

$$\ln(\text{Pe}) := 30 \cdot \text{ETcrop} - (\text{Pe} + \text{Ge} + \text{Wb})$$

The net irrigation requirement is calculated as a function of the average rainfall. The groundwater contribution, Ge, and the water initially stored in the soil have been set to zero.

$$V(\text{Pe}) = \frac{1}{\text{Ep}} \cdot \frac{\ln(\text{Pe})}{1 - \text{LR}}$$

The monthly volume of water required is calculated. The irrigation system efficiency, EP, is assumed to be 100% and the leaching requirement has been set to

$$\text{Vper}(\text{Pe}) = \frac{V(\text{Pe})}{4}$$

The depth in mm of a weekly irrigation event is calculated.

The following models the diffusion into the crop canopy of the TCE which is ponded at the base of the corn.

$$M := 130 \qquad \alpha := .9$$
$$\beta := 1.83 \cdot 10^{-5} \qquad \text{KH} := 1.07 \cdot 10^{5}$$
$$T := 24.4 \qquad R := 8.13$$

The values for molecular weight (g/mol), alpha, beta, Henry's Law constant (dyne-cm/g), temperature(degrees K), and ideal gas constant (J/mole-K) are given.

$$\text{Kint} := \alpha \cdot \beta \cdot \text{KH} \cdot \left[\frac{M \cdot \frac{1}{1000}}{2 \cdot \pi \cdot R \cdot 100^2 \cdot (T + 273.16)} \right]^{\frac{1}{2}}$$

Kint is the exchange constant for the water/air interface and is of the form required to account for the contribution of the interface to the net diffusivity.

$$\text{KA}(x,t) := \text{if}\left(\frac{t}{24} > 1, \text{if}(K(\text{mod}(t,24)) \cdot \psi(x) > 0, K(\text{mod}(t,24)) \cdot \psi(x), .001356), \text{if}(K(t) \cdot \psi(x) > 0, K(t) \cdot \psi(x), .001356) \right)$$

$$\text{KE}(x,t) := \frac{x}{\left(\frac{1}{\text{Kint}} \right) + \sum_{i=1}^{x} \frac{\Delta x}{\text{KA}(i,t)}}$$

KA(x,t) generates a diffusivity in cm2/sec. If the diffusivity from Parmele is zero, the molecular diffusion coefficient for TCE is returned. The equivalent diffusivity is then calculated by evaluating the contributions of the individual layers.

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$$F(C0, t) = Kint \cdot \left(C0 \frac{1}{1000} \cdot exp\left(-\frac{Kint \cdot t \cdot 60 \cdot 60}{.5 \cdot 100} \right) \right)$$

$$Di(x, t) = \int_{6}^{t} KE\left(x, \frac{\tau}{3600} \right) d\tau$$

The variable of substitution and the diffusion equation complete the modeling.

$CL1 := 0, .5 .. 10$

$t1 := 0, 10 .. 500$

$t2 := 400, 410 .. 700$

$MASS(CL2, Pe) := Vper(Pe) \cdot 10 \cdot CL2 \cdot .001$

The mass, MASS, of TCE deposited on the ground per unit area is determined. This calculation assumes that the initial aqueous concentration reaching the corn is given in ug/L (ppb). The volume of irrigation is converted from mm to cm and ug/L is converted from L to cubic centimeters

The concentration in ug/cm3 is evaluated as function of time (Crank,1970:10).

$$CA(CL2, Pe, x, t) := \frac{MASS(CL2, Pe)}{\sqrt{\pi \cdot Di(x, 3600 \cdot (t + 6))}} \cdot exp\left[\frac{-x^2}{4 \cdot Di(x, 3600 \cdot (t + 6))} \right]$$

The following models the leaching of the chemical into the ground.

$\theta := .22 \quad con := 10^{-3} \quad Pe := 140 \quad B := 2.8 \quad z := .5, 1 .. 7$

$CL2 := 1, 10 .. 100 \quad \alpha := .05, .1 .. 1 \quad Kd := 1, 3 .. 20$

$Vi := con \cdot Vper(Pe) \cdot 10$

$t0 := \frac{Vper(Pe)}{Vi}$

The velocity of the infiltration is calculated based on the volume of irrigation and conductivity of the soil.

The time, t0, for all of the water to infiltrate the soil is calculated.

$Vz := \frac{Vi}{\theta} \quad Kp(Kd) := \frac{B}{\theta} \cdot Kd$

$$S(z,t,\alpha,Kd,CL2) = Kp(Kd)\cdot CL2\cdot\theta\cdot .001\cdot \exp\left(-\alpha\cdot Kp(Kd)\cdot\frac{z}{Vz}\right)\cdot\int_0^{\alpha\cdot\left(t-\frac{z}{Vz}\right)} \exp(-\tau)\cdot I0\left[2\cdot\left(\frac{\alpha\cdot Kp(Kd)\cdot z\cdot\tau}{Vz}\right)^{\frac{1}{2}}\right]d\tau$$

$SS(z,t,\alpha,Kd,CL2) = \dfrac{1}{B}\cdot S(z,t,\alpha,Kd,CL2)$ The concentration is formulated in ug TCE per gram of soil.

The amount of TCE in the liquid phase is calculated.

$$C(z,t,\alpha,Kd,CL2) := \frac{S(z,t,\alpha,Kd,CL2)}{Kp(Kd)} + \blacksquare$$

$$CL2\cdot\theta\cdot .001\cdot\exp\left(\frac{-\alpha\cdot Kp(Kd)\cdot z}{Vz}\right)\cdot\exp\left[-\left[\alpha\cdot\left(t-\frac{z}{Vz}\right)\right]\right]\cdot I0\left[2\cdot\left[\alpha^2\cdot Kp(Kd)\cdot z\cdot\frac{\left(t-\frac{z}{Vz}\right)}{Vz}\right]^{\frac{1}{2}}\right]$$

$CS(z,t,\alpha,Kd,CL2) := \dfrac{1}{\theta}\cdot\blacksquare(z,t,\alpha,Kd,CL2)\cdot 1000$ The concentration is formulated in ug TCE per Liter of solution.

The following models the effect of pure water being applied to the crop after irrigation.

The following models the effect of pure water being applied to the crop after irrigation.

$Crain(z,t,\alpha,Kd,CL2) := \dfrac{\blacksquare(z,t,\alpha,Kd,CL2)}{Kp(Kd)} + \blacksquare$

$$Crain(z,t,\alpha,Kd,CL2) := \frac{\blacksquare(z,t,\alpha,Kd,CL2)}{Kp(Kd)} + CL2\cdot\exp\left(\frac{-\alpha\cdot Kp(Kd)\cdot z}{Vz}\right)\cdot\exp\left[-\left[\alpha\cdot\left(t-\frac{z}{Vz}\right)\right]\right]\cdot\blacksquare$$

$$\left[\left[I0\left[2\cdot\left[\alpha^2\cdot Kp(Kd)\cdot z\cdot\frac{\left(t-\frac{z}{Vz}\right)}{Vz}\right]^{\frac{1}{2}}\right]\right] - \exp(\alpha\cdot 100)\cdot I0\left[2\cdot\left[\alpha^2\cdot Kp(Kd)\cdot z\cdot\frac{\left(t-\frac{z}{Vz}-100\right)}{Vz}\right]^{\frac{1}{2}}\right]\right]$$

$CR(z,t,\alpha,Kd,CL2) := \dfrac{1}{\theta}\cdot\blacksquare(z,t,\alpha,Kd,CL2)$

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13. ABSTRACT (Maximum 200 words)

This research developed a methodology for assessment of the exposure of a mature corn crop to trichloroethylene from a contaminated aquifer. The methodology was then applied to the case of Hill AFB to determine the ability of the methodology to provide information about a specific exposure. Current procedures sample for food contamination but do not attempt to predict exposure problems. A review of the potential exposure pathways from the aquifer to the crop was conducted. Based on this review, the exposures due to soil gas and irrigation were modeled. Empirical estimates were used to approximate the expected flux of soil gas vaporizing directly from the aquifer. On the basis of this approximation, the exposure in the air of the crop canopy was mathematically estimated. Analytical models were developed to simulate the amount of the contaminant reaching the crop from two different means of irrigation. The subsequent exposure once the contaminated irrigation water had reached the crop was modeled both in the air of the crop canopy and the soil phase near the root system. The methodology provided insights into which exposure pathways are more important than others and which environmental parameters most influence the amount of exposure.

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